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HAND-BOOK

OF

CHEMISTRY.

BY

LEOPOLD GMELIN.

VOL. VII.

ORGANIC CHEMISTRY,

VOL. I.

GENERALITIES OF ORGANIC CHEMISTRY. — ORGANIC COMPOUNDS CONTAINING TWO ATOMS OF CARBON.

TRANSLATED BY

HENRY WATTS, B.A., F.C.S.

LONDON:
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PREFACE TO THE "ORGANIC CHEMISTRY."

(FOURTH EDITION, 1848.)

At length I have the satisfaction of offering to the Reader the First Volume of the "Organic Chemistry," and at the same time of expressing a confident expectation that the publication of the remaining volumes will proceed without any serious delay.

Having been unable, during the preparation of the inorganic part of the work, to take any account of the yearly increasing additions to the organic division of the science, I found, on commencing this latter portion of the work, that the first thing to be done was to collate the neglected matter.

But the more carefully this was done, the greater appeared the difficulty of revising, co-ordinating and elaborating the mass of matter thus accumulated.

And in the first place, it appeared absolutely necessary to devise a new mode of classifying organic compounds, inasmuch as the arrangement adopted in the former editions could no longer be considered satisfactory. Fortunately, in the interim, thanks to the labours of numerous chemists, at the head of whom Liebig shines conspicuous, the composition of the greater number of organic compounds has been so far made out, that it does not appear too bold an attempt to adopt this character, as the most essential, for the basis of the classification. Moreover, since, in my opinion, carbon is the only constant, and therefore the only essential constituent of organic compounds (pp. 3, 4), it appears most appropriate to arrange them according to the number of carbon-atoms contained in a single

atom of the compound; and since we may assume that, as the number of carbon-atoms increases, the compounds assume a more and more decidedly organic character, whereas a diminution of the number of carbon-atoms brings them nearer to the condition of inorganic compounds, it likewise appears proper, after completing the description of the latter, to begin with those organic compounds which contain the smallest number of carbon-atoms, and proceed regularly from these to the highest,—a mode of arrangement which, though in a different way, has been adopted by Gerhardt in his "Précis."

To carry out this arrangement further, it was necessary to choose between the *Radical-Theory* adopted and developed by Berzelius and most other chemists, and the *Nucleus-Theory* as recently brought into notice by the labours of Laurent, Dumas, and Gerhardt. My reasons for preferring the latter, and introducing it, though with many alterations, into this Hand-book, are fully stated in the text (pp. 9—38).* And now that the first volume is complete, I see no reason to repent of my choice; on the contrary, I am more and more convinced that the Nucleus-Theory, when properly carried out, arranges organic compounds in a natural order, which is as easy of comprehension as the extraordinary variety of the compounds will admit; and although the constitution of many compounds militates at present against the laws of this theory,—a point on which I have been and shall always be solicitous to direct attention,—it is nevertheless scarcely to be doubted that these discrepancies will be reconciled in one way or another, as, indeed, they have already been in several instances. The most recent example of this kind is afforded by Cyanuric acid, $C^6N^3H^3,O^6$. This acid was formerly regarded as tribasic; but since it contains 6 At. oxygen outside the nucleus, it should, according to the Nucleus-

* The balance of probability between the two theories having been somewhat altered by recent investigations (*vid.* pp. 16–18), the translator, in stating the composition of certain newly-discovered compounds (*e. g.* Methylamine, &c., pp. 313–329) has chiefly adopted the formula of the Radical-Theory.

Theory, be bibasic; and such, in fact, it has actually been found to be (*vid.* p. 204). It is precisely because this theory leads to important laws, which enable us to decide *à priori* on the correctness or probability of formulæ deduced from experiment, that it is preferable to a theory before whose judgment-seat—in the absence of laws—almost any composition of an organic compound appears possible, and consistent with its properties whatever they may be; such a theory as the latter cannot indeed be easily confuted by any formula deduced from experiment. Lastly, if it be objected to the Nucleus-Theory that it requires certain hypotheses, we may remark that hypotheses must be admitted in any theory that can be formed respecting compounds so enigmatical as those of the Organic Kingdom; least of all are they wanting in the Radical-Theory, whose numerous radicals, anhydrous acids, and copulæ, are, for the most part, not known in the separate state.

The peculiar difficulty in classifying organic compounds according to the Nucleus-Theory, lies, however, not so much in the theory itself, as in the diversified character of our knowledge respecting many organic compounds. For of many compounds the constitution is yet uncertain; of others we know, indeed, the empirical formula, but are in doubt respecting the rational formula. For example: should *Oxalic Acid* dried *per se* be regarded as C^2HO^4, or as $C^4H^2O^8$, and does it belong to the 2-carbon or the 4-carbon group? Is *Acetone* a primary compound $C^6H^6O^2$, or a copulated compound $C^4H^4O^2,C^2H^2$, and does it belong to compounds with 6 or 4 At. carbon? In some of these doubtful cases, that view has been taken which appears the most probable; in others, the doubtful compound has been annexed in an appendix to those with which it seems to be most closely related. The latter course has also been pursued with all compounds of unknown constitution, of which the subsequent volumes will, unfortunately, include a greater number than the present. With the further investigation of the composition and decompositions of organic compounds,

these imperfections will gradually disappear, and the system here put forward, together with the theory on which it is founded, will be perfected and at the same time considerably altered; but I shall be satisfied, if it prove to be correct and consistent in its principal features.

In the stoïchiometric calculations contained in this and the following volumes, the more exact determinations recently made of the atomic weights of certain elements have been adopted; thus, Bromine = 80 (instead of 78·4); Iron = 28 (instead of 27). Should any other *important* corrections of this kind be published, they will likewise be adopted in the subsequent parts of the work.

THE AUTHOR.

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(VOL. I. OF ORGANIC CHEMISTRY.)

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PART II.

CHEMISTRY OF ORGANIC COMPOUNDS,

OR

ORGANIC CHEMISTRY.

THE bodies of the organic kingdom are distinguished, in their most complete state, from those of the inorganic kingdom:

1. By their inherent vital force.
2. By a peculiar structure, internal and external.
3. By being composed—for the principal and most important part at least—of chemical compounds quite peculiar to them, called *Organic Compounds*, or *Proximate Principles of the Organic Kingdom*, which occur in the bodies of plants and animals, partly mixed and partly combined, both with one another, and with certain inorganic compounds.

The proximate principles into which an organic body may be resolved, either by mechanical or by chemical means, are partly inorganic, such as water, carbonic acid, and other mineral acids; partly organic. When the latter are of such a nature, that any attempt to decompose them further leads to the formation of decomposition-products, which when reunited, produce something totally different from the substance originally decomposed—they are regarded as *Primary*, or *Elementary Organic Compounds*.

Organic Chemistry considers:

1. The organic compounds occurring in the bodies of plants and animals, together with the combinations which they form with each other and with inorganic bodies: *Chemistry of Organic Compounds in the most restricted sense.*
2. The composition of plants and animals and of their parts, formed of these compounds and of inorganic substances: *Chemical Botany and Zoology.*
3. The chemical changes which occur in these bodies, so long as they are subject to the influence of the vital force: *Chemical Physiology of Plants and Animals.*

Subdivision I.

PRIMARY ORGANIC COMPOUNDS.

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I. CONSTITUTION OF ORGANIC COMPOUNDS.

1. *Components.*

Organic compounds do not by any means differ from those of the inorganic kingdom in the elements of which they are composed. The elements by which the former are produced are likewise found in the latter; but while all the elements can combine to form inorganic compounds, only a limited number of them are capable of entering into compounds of the organic class. All organic compounds contain carbon; most of them contain hydrogen and oxygen; a few contain nitrogen; and a very few contain phosphorus, sulphur, iodine, bromine, chlorine, &c. From this small number of elements, there are formed several thousand organic compounds, distinguished from one another, either by the different nature and relative quantities of their constituents, or, when the composition is the same, by isomeric, metameric, and polymeric relations.

Carbon is the only element which is essential to organic compounds. Every one of the other elements may be absent from particular compounds; but no compound, which in all its relations deserves the name of organic, is destitute of carbon. Accordingly, ammonia and ammonium

cannot properly be regarded as organic compounds; it is true that sal-ammoniac, considered as chloride of ammonium, NH^4Cl, is sometimes compared with hydrochloric ether, regarded as chloride of ethyl, C^4H^5Cl, &c.; but these two compounds do not really exhibit the resemblance thus ascribed to them, their decompositions showing, indeed, that they contain chlorine in totally different states of combination.

If we were to regard as organic, those carbon-compounds which have hitherto been classed among inorganic substances, *viz.* carbonic oxide, carbonic acid, sulphide of carbon, phosgene, cast-iron, &c., we might define *Organic Compounds* simply as the *Compounds of Carbon.*

But organic compounds are still further distinguished by containing more than one atom of carbon.—To this supposition we are often led by the proportion in which the elements are combined. Thus, cyanogen contains 14 pts. nitrogen and 12 pts. carbon; hence its formula is C^2N. In other compounds, the same conclusion is deduced from the proportion in which they combine with other substances. Thus, acetic acid contains equal numbers of atoms of carbon, hydrogen, and oxygen, and might be regarded as CHO; but 1 At. potash requires for its neutralisation a quantity of acetic acid corresponding to the formula $C^4H^4O^4$.

Hence the term *Organic Compounds* includes *all Primary Compounds containing more than one atom of Carbon.*—By primary compounds we mean such as are not, like bicarbonate of potash, made up of other compounds.

Hydrogen occurs in nearly all organic compounds. Many of them consist of carbon and hydrogen alone; and in these hydro-carbons, one atom of carbon is combined with not less than $\frac{1}{3}$ At. and not more than 2 At. of hydrogen. Many others contain one or several other elements in addition.

There is no organic compound consisting merely of carbon and oxygen; but very many organic compounds contain oxygen together with carbon and hydrogen or other elements. It is true that the hypothetically anhydrous oxalic and croconic acids are composed of C^2O^3 (or C^4O^6) and C^5O^4; but these compounds are not known in the separate state, their existence being merely hypothetically assumed by certain chemists. The quantity of oxygen in organic compounds is never sufficient to convert all the carbon into carbonic acid and at the same time all the hydrogen into water. Oxalic acid, which contains a larger proportion of oxygen than any other organic compound, is composed, when dried as far as possible, of C^2HO^4; and it is evident that to form $2CO^2$ and HO, one more atom of oxygen would be required.

There are a few organic compounds, and only a few, consisting entirely of carbon and *Nitrogen*, such as Cyanogen$=C^2N$, and Mellon$=C^6N^4$. Others contain hydrogen, in addition, as Nicotine$=C^{10}H^7N$; Aniline$=C^{12}H^7N$. Others again contain both hydrogen and sulphur, in addition to carbon and nitrogen; thus Oil of Mustard$=C^8H^5NS^2$; and very many consist of carbon, hydrogen, oxygen, and nitrogen, such as the crystalline alkaloids, animal products of nutrition, &c., *e. g.*, Narcotine$=C^{46}H^{25}NO^{14}$; Protein$=C^{40}H^{31}N^5O^{12}$.

There are likewise a few organic compounds containing nothing but carbon and *Chlorine*, as C^2Cl^2, C^2Cl^4, C^4Cl^6.—Much more frequently, *Chlorine*, *Bromine*, and *Iodine* occur in such compounds, associated with other elements besides carbon.

An organic compound may contain from two to six elements. Cyanogen=C^2N; Wood-spirit=$C^2H^4O^2$; Urea=$C^2H^4N^2O^2$; Chloro-dibromanilin=$C^{12}H^4Br^2ClN$. Albumen (according to Mulder)=$C^{400}H^{310}N^{80}O^{120}S^3P$ =$10(C^{40}H^{31}N^5O^{12})+S^3+P$. The number of atoms of carbon and hydrogen in primary organic compounds may amount to about 70; but the number of oxygen-atoms never exceeds 28, and that of the other atoms amounts to only 1 to 6.

2. *Even numbers of the Elementary Atoms.*

Nearly all organic compounds contain an even number of carbon-atoms, either 2 or 4, 6, 8, 10, &c., up to 68. In the following, however, the number of carbon-atoms is uneven; Mesoxalic acid=C^3HO^5; Croconic acid=C^5HO^6; Citraconic acid=$C^5H^2O^3$; Itaconic acid and Lipic acid =$C^5H^3O^4$; Pyrotartaric acid=$C^5H^4O^4$; Rhodizonic acid=C^7HO^7(?); Gallic acid=$C^7H^3O^5$; and Pimelic acid=$C^7H^6O^4$. These exceptions may be got rid of by doubling, as Gerhardt does, the atomic weights of these acids, and consequently the number of their carbon-atoms, whereby a monobasic acid is rendered bibasic, and a bibasic acid (like gallic acid) becomes quadrobasic. In some of these acids, the duplication appears to be justified by their behaviour with salifiable bases, while in others it is merely introduced to make the number of carbon-atoms even. It is remarkable that 5 is almost the only uneven number that the carbon-atoms can assume. In some of the alkaloids, also, the analyses hitherto made give uneven numbers of carbon-atoms, *e. g.*, in Pseudomorphine, Codeine, Emetine, and Sanguinarine. Considering, however, the difficulty of such analyses, as well as the circumstance that these compounds contain from 38 to 40 atoms of carbon, so that a slight error in determining the quantity may easily make a difference of one or more in the number of carbon-atoms, it may reasonably be hoped that these exceptions will disappear on further investigation.

The sum of the atoms of the other elements which are associated with carbon in an organic compound, is likewise almost always an even number.

All hydrocarbons contain even numbers of hydrogen-atoms: C^2H^2, C^4H^4, $C^{12}H^6$, $C^{16}H^8$, $C^{20}H^8$, $C^{20}H^{16}$, $C^{32}H^{32}$, &c. [except the radicals C^2H^3, C^4H^5, $C^{10}H^{11}$, &c. (W.)]

Similarly all the compounds of carbon with chlorine contain even numbers of chlorine-atoms: C^2Cl^2, C^4Cl^6.

But in Cyanogen, C^2N, the number of nitrogen-atoms is uneven.

In compounds containing two or more elements besides carbon, each of the elements sometimes occurs in an even number of atoms. Even numbers occur with the greatest frequency in the oxygen and sulphur atoms. In other cases, however, it is only by adding together the atoms of the several elements that an even number is obtained. Thus, on the one hand: Acetic Acid=$C^4H^4O^4$; Benzoic acid=$C^{14}H^6O^4$; Lactic acid =$C^6H^6O^6$; Alcohol=$C^4H^6O^2$; Mercaptan=$C^4H^6S^2$.—On the other hand, Ether=C^4H^5O; and analogous to this are: C^4H^5Cl; C^4H^5S; C^4H^3ClSO; Pyrogallic acid=$C^6H^6O^3$; Nicotine=$C^{10}H^7N$; Aniline=$C^{12}H^7N$; Coniine =$C^{16}H^{15}N$; Leucol=$C^{18}H^7N$; Indigo=$C^{16}H^5NO^2$; Chloral=$C^4HCl^3O^2$; Bromoform=C^2HBr^3; Bromiodoform=C^2HI^2Br; Chlorophenissic acid= $C^{12}H^3Cl^3O^2$.

In certain other compounds, however, no even numbers are obtained, even by adding together all the atoms combined with the carbon. This is the case with Indigo-white=$C^{16}H^6NO^2$; hence Laurent & Gerhardt, in

order to make the numbers even, and without assigning any other reasons, double the atomic weight of this compound, making it = $C^{32}H^{12}N^2O^4$. This exception is likewise exhibited by certain organic acids: Oxalic acid = C^2HO^4; Mellitic acid = C^4HO^4; Tartaric and Racemic acid = $C^4H^3O^6$; Mucic acid = $C^6H^5O^8$; Saccharic acid = $C^6H^5O^8$; Ellagic acid = $C^{14}H^3O^8$, and a few others. But the high boiling points of most of these acids, and their deportment with salifiable bases, render it probable that their atomic weight should be doubled, whereby they would be converted from monobasic to bibasic acids. Thus: Oxalic acid = $C^4H^2O^8$; Mellitic acid = $C^8H^2O^8$.

This law of the *Even Numbers of Atoms* proposed by Laurent & Gerhardt is expressed by them as follows [adopting the atomic weights of the elements as given in this Hand-book]: If the atomic weight of an organic compound be fixed at such an amount that its vapour shall be di-atomic [I, 52—67], or (according to the usual mode of expression, which will be explained in speaking of the properties of organic compounds,) that one atom of the compound in the form of vapour shall occupy 4 volumes, then the following quantities will be divisible by 2: —(1) The number of Carbon-atoms in the compound;—(2) The sum of the atoms of Hydrogen, Iodine, Bromine, Chlorine, Nitrogen, and Metal; —(3) The sum of the atoms of Oxygen, Sulphur, Selenium, and Tellurium.

This mode of stating the law removes many exceptions, which seem to present themselves at first sight. If the formula of ether be C^4H^5O, the number of atoms of hydrogen and of oxygen will be uneven. According to the preceding law, however, the atomic weight of every organic compound must be so established that its vapour may be di-atomic, or that one atom of it may occupy 4 volumes of vapour. Hence, since ether = C^4H^5O gives but 2 volumes of vapour, its formula must be altered to $C^8H^{10}O^2$, and then it will give 4 volumes of vapour, and the number of atoms, both of hydrogen and oxygen, will be even. Finally, although this law is still subject to certain exceptions, some of which, especially that of cyanogen = C^2N, cannot easily be got rid of, it is, nevertheless, well worthy of consideration, since it holds good in the greater number of cases. It appears to be due to the tendency of the atoms to approach one another as nearly as possible, whence there results a more or less symmetrical arrangement, which could not so well take place if the numbers of atoms were uneven.

3. *Mode of Combination of the Elements in Organic Compounds.*

Since the products of the vegetable and animal kingdoms have been made the subjects of chemical investigation, it has been observed that a chemical difference exists between these products and those of the mineral kingdom; but the nature of this difference has never been sufficiently made out. At first, chemists were contented with ascribing the difference to variety of origin, inasmuch as organic compounds are formed in plants and animals, while inorganic compounds occur in inanimate nature, or are produced artificially. But since more recent investigations have shown that certain compounds, obviously of organic nature, may be artificially produced from inorganic materials, this distinction is no longer tenable.

Berzelius (*Ann. Phil.* 4, 323,) formerly attempted the following mode of distinction. All inorganic compounds are binary; all organic compounds, ternary, quaternary, quinary, or senary. Thus, an inorganic compound, when it contains more than two elements, may always be divided into two parts, from which again it may be recomposed, each

of these parts being either simple, or itself divisible into two parts, and so on. Thus KO,SO^3 is the binary compound of KO and SO^3, the first of these, KO, being composed of K and O, and the second, SO^3, of S and O^3. Organic compounds, on the contrary, contain more than two elements; and these are directly combined into a whole, without being previously united into binary compounds. Thus alcohol, $C^4H^6O^2$, is a ternary compound, and cannot be resolved into any two compounds, capable of reproducing alcohol by their union, &c.

Since, however, it has been found that many compounds, which must necessarily be regarded as organic, such as oil of turpentine, and many other volatile oils, &c. consist of only two elements, and are, therefore, binary compounds, this mode of distinction can no longer be maintained.

Many other chemists, on the contrary, regarded organic compounds as formed by the union of carbonic oxide, carbonic acid, water, marsh-gas (C^2H^4), olefiant gas (C^4H^4), and other similar binary compounds among themselves. Thus Gay-Lussac regarded alcohol, $C^4H^6O^2$, as a compound of olefiant gas, C^4H^4, with 2HO; while Döbereiner regarded it as a compound of 1 At. carbonic acid with 3 At. marsh-gas, which he viewed as an inorganic compound, CH^2. Persoz (*Chim. molecul.* 866,) attributed to acetic acid, $C^4H^4O^4$, the formula C^2H^3,CO,CO^2,HO, and altered in a similar manner the formulæ of most of the other acids, assuming in them 1 At. water, 1 At. carbonic acid, and 1 At. carbonic oxide ready formed. Mitscherlich is inclined to regard benzoic acid, $C^{14}H^6O^4$, as a compound of benzoyl, $C^{12}H^6$, and $2CO^2$. But all these assumptions are founded merely on the possibility of transforming organic compounds, by certain modes of decomposition, into water, carbonic oxide, carbonic acid, &c., which compounds, however, do not really exist in the organic bodies, excepting by their elements, but are actually produced in the decomposition; in a word, they are not educts but products of decomposition, and cannot by any means be made to unite so as to reproduce the original compound. Moreover, this mode of view admits of numerous hypotheses respecting the same compound, all equally arbitrary, and contributes nothing to a general view of the constitution of organic compounds.

The more exact knowledge of the composition and decompositions of organic compounds, obtained by the labours of the most distinguished chemists in recent times, has caused the above-mentioned views to be for the most part abandoned, and has substituted for them two important theories, which at present may be said to contend for the victory, and moreover, have received particular modifications according to the views of their individual adherents.

The first of these theories is the *Radical-Theory*, or *Binary-Theory* of Berzelius; the second, the *Nucleus-Theory* of Laurent, which, however, is intimately connected with the *Type-Theory*, or *Substitution-Theory* of Dumas.

The elementary analysis of an organic compound gives merely its *Crude Chemical Formula*, or *Empirical Formula*, which simply expresses the numbers of atoms of the constituents. Thus, the empirical formula of acetic acid dehydrated as far as possible *per se*, is $C^4H^4O^4$. Such a formula, however, does not inform us *in what manner* these 12 atoms are united together. To denote this is the object of the *Rational Formula*. But as the atoms are invisible, and consequently their mutual arrangement cannot be made the subject of direct observation, it is evident that the rational formula can only be hypothetically established with more or

less probability, from the mode of formation and decomposition of aceic acid, and by comparing that substance with other compounds. The rational formula, according to the radical-theory, is, *e. g.*, C^4H^3+O+HO, *i e.* Oxyde of Acetyl with Water, acetyl, C^4H^3, being the radical. The nucleus theory gives for the rational-formula, either $C^4H^4+O^4$, *i. e.*, Ethylene (olefiant gas) + 4 Oxygen, ethylene being the nucleus,—or C^4H^3O, HO^3 (*vid.* p. 33).

A. Radical-theory.

According to Berzelius (*Pogg.* 49, 289; also *Ann. Pharm.* 31, 1; further *Lehrb.* Aufl. 5, 1, 672), the peculiar phenomena exhibited by living plants and animals are due, not to a vital force, or to several such forces, but to certain circumstances connected together in a peculiar manner, under which the ordinary forces of nature are excited to activity in organic matter. Hence the mode of combination of the elements in organic compounds may be inferred from that which exists in the inorganic kingdom. As inorganic compounds consist of an electro-positive radical united with oxygen or other electro-negative body, *e. g.*, SO^3, HCl, KCl, so likewise do organic bodies; with this difference, however, that the radicals of inorganic compounds are simple, while those of organic bodies are compound. This is the most important of all distinctions between organic and inorganic compounds. Such compound radicals are either compounds of carbon and hydrogen, as Formyl=C^2H; Methyl=C^2H^3; Acetyl=C^4H^3; Ethyl=C^4H^5, &c.; or of carbon, hydrogen, and nitrogen, as Indene=$C^{16}H^5N$; or of carbon, hydrogen and arsenic, as Cacodyl=C^4H^6As; or of carbon, hydrogen and sulphur. There are therefore, binary, ternary, and perhaps also quatenary radicals to be distinguished.—All the so-called electro-negative bodies, as O, Cl, Br, I, are excluded from the radicals.—(Liebig and Wöhler include among the radicals certain oxidized hydrocarbons, as Benzoyl=$C^{14}H^5O^2$, inasmuch as bitter almond oil=$C^{14}H^6O^2$, may be regarded as hydride of benzoyl=$C^{14}H^5O^2$,H, and this 1At. H, may be replaced by 1At. O, Cl, or Br; but Berzelius rejects the supposition of oxygen existing within the radical.)

With these radicals, which may be compared with metalloidal compounds, such as ammonium, the electro-negative elements, oxygen, sulphur, chlorine, bromine, &c., unite in different numbers of atoms, and form oxides, acids, sulphides, bromides, chlorides, &c. The compounds thus formed are capable of uniting either with one another or with inorganic compounds. In inorganic compounds, one atom of a radical appears to be capable of uniting with not more than 7 At. oxygen, *e. g.*, Perchloric acid=ClO^7; and the same law appears to hold good with regard to organic compounds.

Radicals consisting of carbon and hydrogen have names ending in *yl*, from ὑλη, *matter;* those which contain carbon and nitrogen generally have names ending in *an* or *anogen*, as Cyanogen; and the names of those containing carbon, hydrogen and oxygen, end in *ene*, as Indene.

Many oxides and acids contain water so intimately combined, that it cannot be separated from them by heat. In acids, this hydration-water or basic water supplies the place of a base, and is not given off till a strong salifiable base, such as potash, lead-oxide, or silver-oxide, is introduced, and a degree of heat applied, varying according to the nature of the acid, in which case, after the water has been expelled, a compound of the true anhydrous acid with the base remains behind. Thus, the lowest state of hydration in which acetic acid can be obtained is that of

glacial acetic acid, $C^4H^4O^4$; but its compound with potash, when thoroughly dried $=KO,C^4H^3O^3$. Hence glacial acetic acid contains 1 At. basic water; it is a hydrate of acetic acid, and must be expressed by the formula $HO,C^4H^3O^3$. The true anhydrous acetic acid is therefore $=C^4H^3O^3$, and consists of a radical called Acetyl, C^4H^3, united with 3 At. oxygen. If this acetyl be denoted by Ac, the similarity between the compounds of an organic and an inorganic acid becomes apparent; Oil of vitriol $=HO,SO^3$; Acetic acid $=HO,AcO^3$; Sulphate of potash $=KO,SO^3$; Acetate of potash $=KO,AcO^3$. (Berzelius.)

According to this theory, every organic body is either a compound radical, or a compound of such a radical with oxygen or other electro-negative element, and frequently also with water. Organic chemistry is therefore the *Doctrine of Compound Radicals.* The radical is the constant element in a series of compounds. In such a compound, it is necessary, on the one hand, that the radical be replaceable by other bodies, and, on the other, that the elements combined with the radical be capable of being expelled by a corresponding number of atoms of other elements. The radicals, for the most part, cannot be obtained in the separate state, because they readily decompose when separated from other bodies; but anhydrous nitric acid is unknown in the separate state, and yet its existence is assumed.* (Liebig, *Ann. Pharm.* 25, 2.) Radicals are capable of taking up more than 7 atoms of oxygen; thus Kinic acid contains 9 At., and Ulmic acid, 7 At. of oxygen. (Liebig, *Ann. Pharm.* 31, 35.)

The radicals are compounds in which all the properties of the elementary bodies are reproduced. Several of them, as cyanogen, play the part of chlorine or oxygen [Berzelius (*Lehrb.* 1, 672) places cyanogen amongst inorganic compounds]; others such as methyl, benzoyl, &c., resemble the metals. In mineral chemistry, the radicals are simple; in organic chemistry, they are compound. (Liebig and Dumas, *J. pr. Chem.* 14, 298.)

The majority of chemists are in favour of the radical theory. Liebig adopts it in his works, with certain modifications, but nevertheless regards the assumption of the substitution of chlorine for hydrogen as admissible, thereby departing from the rigid electro-chemical theory of radicals.

The admission of this theory is attended with the following difficulties:—

The doctrine of compound radicals, if consistently followed out, as is done by Berzelius (*Lehbr.* Aufl. 5. 1, 623—660), places many acids of obviously organic character in the list of inorganic acids. Thus oxalic acid, dried *per se*, has the composition C^2HO^4; but this compound is supposed to contain 1HO, which is given off when the acid combines with PbO under the influence of heat; there then remains the compound C^2PbO^4, or, according to Berzelius, PbO,C^2O^3; *i.e.*, a compound of lead-oxide with an oxalic acid deprived of its basic water,—a compound not known in the separate state, and having merely a hypothetical existence. (Acids supposed to exist in such a state will be called, in this Hand-book, *hypothetically anhydrous acids.*) Since now, according to this view, the true oxalic acid is C^2O^3, it is a compound of oxygen, not with a compound but with a simple radical, C^2, and consequently belongs to the class of inorganic acids. It must therefore take its place among the oxygen-compounds of carbon, between carbonic oxide and carbonic acid, CO, C^2O^3, CO^2, corresponding to the oxides of manganese, for example,

* Respecting anhydrous nitric acid, *vid.* II., 389; on the other hand, the number of organic radicals known to exist in a separate state is continually increasing. [W.]

MnO, Mn^2O^3, MnO^2. Now there is no known example of a compound of any substance with a smaller quantity of oxygen, forming a stronger acid than a compound of the same substance with a larger quantity of oxygen. But oxalic acid is one of the strongest of known acids, and carbonic acid one of the weakest!—For the same reason, Berzelius has included among inorganic acids, the chloracetic, mellitic, mesoxalic, croconic and rhodizonic acids; which, when dried *per se*, are composed of $C^4HCl^3O^4$; C^6HO^4; C^3HO^5; C^6HO^6; C^7HO^7;—but in the hypothetically anhydrous state have the formulæ: $C^4Cl^3O^3$; C^6O^3; C^3O^4; C^5O^4; and C^7O^6. These acids likewise contain less oxygen than carbonic acid, and some of them less even than carbonic oxide; but nevertheless they are stronger acids than carbonic acid. Lastly, chloracetic acid bears the most intimate relation to acetic acid, $C^4H^4O^4$. Acetic acid is converted by chlorine into chloracetic acid, and the latter is reconverted into acetic acid by the action of potassium and water. The two acids resemble one another most closely, both in themselves and in their salts. Chloracetic acid forms with silver-oxide a soluble salt, without any precipitation of chloride of silver; whereas chlorine, in all the inorganic compounds in which it forms the electro-negative element, yields with silver-solutions a precipitate of chloride of silver.

Löwig (*Chemie der org. Verbindungen*, Aufl. 2. B. 1, 18) endeavours to remove this difficulty by assuming the existence of *singular* radicals in certain compounds, in addition to the ordinary binary, ternary, and quaternary radicals. In these singular radicals, two or more atoms of carbon are united into a compound atom. Hypothetically anhydrous oxalic acid, C^2O^3, is formed by the union of a compound radical, *Oxatyl*, C^2, consisting of two simple atoms of carbon, with 3 At. oxygen. Hence oxalic acid, C^2O^3, bears to carbonic acid, CO^2, not the relation which hyposulphuric acid, S^2O^5, bears to sulphuric acid, SO^3, but that which sulphuric acid, SO^3, bears to sulphurous acid, SO^2; for the two atoms of carbon, which in the oxalic acid are combined with the oxygen, must be regarded as an indivisible and quasi-simple atom, whereas in hyposulphuric acid, the two atoms of sulphur must be supposed to be separate. For this assumption there is no foundation whatever; for oxalic acid is resolved into CO and CO^2 as easily as hyposulphuric acid into SO^2 and SO^3; the inseparability of the carbon-atoms is by no means apparent. We might, indeed, with equal reason, regard S^2O^5, Fe^2O^3, &c., as organic compounds. The part of this view which is probably correct, but which is not further noticed by Löwig, consists in this,—that in oxalic acid, and the other acids just mentioned, carbon forms the radical, and enters with more than one atom. But instead of assuming that these several atoms of carbon unite (by cohesion) into a compound atom, it is perhaps better to suppose that the carbon-atoms have, by virtue of their affinity, so disposed themselves among the other atoms of the organic compound, that the heterogeneous atoms touch one another in as many points as possible. But this view is not consistent with the radical-theory.

In the binary theory, there are two kinds of radicals to be distinguished.

1. A few, such as cyanogen, C^2N, sulpho-cyanogen, C^2NS^2, mellon, C^6N^4, &c., must be regarded as compound salt-radicals, which in their various relations, resemble chlorine, and like that body, form compounds with hydrogen, metals, &c. They are classed among organic compounds, not, indeed, by Berzelius, but by most of the advocates of the binary

theory; and inasmuch as most of them have been obtained in the separate state, their existence is undeniable.

2. The other radicals, amounting to some hundreds, may be regarded as compound metals analogous to ammonium, and, like that substance, form oxides with a small quantity of oxygen, acids with a larger quantity, chlorides with chlorine, &c. Of these radicals, the only one which is known in the separate state, is Cacodyl, C^4H^6As; all the rest have a merely hypothetical existence, and there is no known method of separating them from their compounds;* in all the reactions to which these compounds are subjected, we obtain other products, but not the desired radicals. This circumstance is ascribed to the facility with which these radicals decompose when in the separate state; but we should scarcely expect to find this easy decomposibility in compounds of so simple a character as C^2H, C^2H^3, C^4H, C^4H^3, C^4H^5, &c. Indeed, we are acquainted with many other compounds of carbon and hydrogen, which exist in the separate state, and are by no means prone to decomposition, such, for instance, as C^2H^4, C^4H^4, $C^{12}H^6$, $C^{14}H^8$, $C^{16}H^8$, $C^{20}H^8$, $C^{20}H^{16}$, $C^{32}H^{32}$, &c. But not one of these compounds, all of which are capable of existing in the uncombined state, is a radical; for they all contain even numbers of atoms, and, according to the radical-theory, must be regarded as compounds of 1 At. H with a radical, such as C^2H^3, C^4H^3, $C^{12}H^5$, $C^{14}H^7$, $C^{16}H^7$, $C^{20}H^{15}$, $C^{32}H^{31}$, &c. The supposed radicals contain uneven numbers of atoms; and this is the reason, not that they are so easily decomposed and cannot be obtained in the separate state, but that the greater number of them have really no existence. The development of the constitution of organic compounds from such radicals is therefore a pure fiction, whereby the simple numerical relations presented by nature, are unnecessarily complicated.

If ether, C^4H^5O, be regarded as oxide of ethyl$=C^4H^5+O$, and hydrochloric ether, C^4H^5Cl, as chloride of ethyl $= C^4H^5+Cl$, then the camphor-like compound which oil of turpentine, $C^{20}H^{16}$, forms with hydrochloric acid, must also be regarded as a compound of the radical $C^{20}H^{17}$ with chlorine $= C^{20}H^{17}Cl$ (or $C^{20}H^{15}Cl+H^2$, *Gm.*). Similarly with oil of lemons, &c.—producing, in fact, very complicated numerical relations.

These chlorine-compounds should be analogous to the metallic chlorides; but the true metallic chlorides, as well as chloride of ammonium $= NH^4,Cl$, immediately throw down chloride of silver from a solution of that metal; while, on the other hand, these compounds which, in the binary theory, are regarded as compounds of chlorine with organic radicals, do not precipitate silver-solutions, so long as they remain undecomposed; the chlorine must therefore be contained in them in a totally different manner.

Even if organic compounds are to be regarded as analogous to inorganic compounds, there is, at all events, no necessity for placing chlorine outside the radical, merely because it is regarded as more electronegative; for, in chloric acid and the other oxygen-acids of chlorine, it actually plays the part of a radical. Similarly with bromine, iodine, and sulphur. The supposition of Berzelius that chlorine always exists in these compounds outside the radical, leads, in many cases, to the assumption of very complicated formulæ. Moreover, compounds which resemble each other very closely are, by the same theory, placed very wide apart. Thus ether, C^4H^5O, belongs, as the oxide of ethyl, to the ethyl-series;

* The recent discovery of stibethyl, stibmethyl, &c., by Löwig & Schweitzer, and the isolation of the alcohol-radicals by Frankland & Kolbe, afford a sufficient answer to this statement, and to the objections founded thereon. [W.]

and by the successive action of chlorine, it may be converted into C^4H^4ClO, $C^4H^3Cl^2O$, and C^4Cl^5O. The second of these compounds is regarded by Berzelius as a compound of 1 At. of hypothetically anhydrous acetic acid with 1 At. of perchloride of acetyl: $3(C^4H^3Cl^2O)=C^4H^3O^3+2(C^4H^3Cl^3)$. On the composition of the second and third compounds, Berzelius has given no opinion; the last $= C^4Cl^5O$, should, according to the principles of the binary theory, be classed among inorganic compounds.

With respect to the organic acids, the number of which amounts to some hundreds, the binary theory is compelled to assume two particular kinds of hypothetical compounds. For since, according to this theory, an acid, when perfectly dried *per se*, still retains a number of atoms of intimately combined water equal to the number of atoms of base which it takes up to form a normal salt (so that a monobasic acid contains 1 At. basic water, a bibasic acid 2 At., &c.), it follows that, besides the acid in its actually driest state, there must likewise exist a hypothetically anhydrous acid, and this again consists of a hypothetical radical united with oxygen. Thus, according to the binary theory, acetic acid, when dehydrated as far as possible, $= C^4H^4O^4=HO,C^4H^3O^3$; and this hypothetically anhydrous acid, $C^4H^3O^3$, which cannot by any known process, be obtained in the separate state, is itself composed of acetyl, C^4H^3, which likewise we are unable to prepare in the free state, and 3 atoms of oxygen.*

Similar observations apply to the greater number of organic acids.

It is indeed alleged that some at least of these acids, viz. the maleic, fumaric, lactic, tartaric, succinic, phthalic, and camphoric acids, may actually be obtained in the state to which the term *hypothetically anhydrous* is above applied. But it may be shown that these compounds, though they certainly have the composition of the hypothetically anhydrous acids, are in reality not acids at all, and can only be brought back to the state of acids by the long continued action of water.

Thus, lactic acid dried at $100°=C^6H^6O^6$; when combined with oxide of lead and dried, it yields a salt, whose composition, according to the binary theory, is expressed by $PbO,C^6H^5O^5$; hence, $C^6H^5O^5$ is hypothetically anhydrous lactic acid. If now lactic acid be heated alone in a retort to 130°, as long as water continues to go off, there remains a pale yellow, solid, easily fusible residue, which is the hypothetically anhydrous acid $=C^6H^6O^5$. This substance, however, has an extremely bitter taste (that of lactic acid is purely and strongly sour); it is quite insoluble in water (lactic acid is very soluble), but dissolves readily in alcohol and ether. By long contact or by boiling with water, and likewise by the action of aqueous alkalis, this substance is dissolved and reconverted into ordinary lactic acid. Similar differences, so far as the matter has yet been examined, are exhibited by the rest of the above-mentioned acids in this peculiar state, produced by strongly heating the fixed acids alone, or the volatile acids with phosphoric acid; hence Laurent no longer regards them as acids, but distinguishes them by the name of *Anhydrides*. When the lactic anhydride, $C^6H^5O^5$, which remains in the retort, is heated to 250°, it gives off a further quantity of water, and is converted into *Lactide*, $C^6H^4O^4$, a neutral, fusible compound, which volatilizes without decomposition, is at first but slightly soluble in hot water, and partly crystallizes out unaltered on cooling, but when sub-

* Anhydrous acetic acid and likewise anhydrous benzoic and cuminic acids have lately been obtained by Gerhardt (*Chem. Soc. Qu. J.* 5, 127, 1226). [W.]

jected to the action of water for a longer time, is reconverted into ordinary lactic acid. Hence, according to the binary theory, if consistently carried out, it would follow that lactic acid formed at 100° is a compound of 1 At. lactide, with 2HO, its formula being $C^6H^4O^4 + 2$ Aq. But this conclusion is opposed to the fact, that lactate of zinc=ZnO,$C^6H^5O^5$, gives off no more water, even at 250°. Since then, according to the hypothesis of the radical theory, lactide does not pre-exist in lactic acid, but is produced when 2H and 2O contained in it, unite in the form of water and escape, it may in the same manner be maintained, that the hypothetically anhydrous lactic acid, $C^6H^5O^5$, does not pre-exist in the acid $C^6H^6O^6$, but is produced when 1H and 1O unite and form water. In both cases, in short, the water is not an educt but a product; and when these bodies, by contact with water, are gradually reconverted into the acid, $C^6H^6O^6$, they do not take up the water as a whole, but the elements of water.*

B. Nucleus-theory.

Gay-Lussac found that wax, when treated with chlorine gas, takes up a number of measures of that gas equal to the number of measures of hydrogen which are taken from it by another portion of the chlorine. Dumas afterwards observed the same phenomenon in oil of turpentine; and as a consequence of this and other investigations, he first developed, in 1834, his theory of *Substitution*, which, after undergoing numerous alterations in the further progress of his researches, led him, in 1840, to the *Theory of Types*. On this theory he says, in 1840 (*Ann. Chim. Phys.* 73, 73): Compounds are to be regarded as planetary systems in which the atoms are held together by affinity. If an atom of one substance is replaced by an atom of another, the system remains the same, In such a change, a simple atom may be replaced by a compound atom, without any alteration of the general constitution. If the substitution takes place in equal numbers of atoms, and the configuration of the atoms remains unaltered, the new compound belongs to the same type as the old. Thus, acetic acid, $C^4H^4O^4$, and chloracetic acid, $C^4HCl^3O^4$, belong to the same type, &c. In 1835, and the following years, Laurent, in the course of his investigations, first of napthaline, then of olefiant gas (in conjunction with Regnault), and of numerous other compounds, discovered a variety of products, in which the hydrogen was replaced by an equal number of atoms of chlorine or bromine. He thereby confirmed and developed the theory of substitution, and, in 1837, first put forth, in a dissertation, his theory of nuclei, which he afterwards more completely developed, in the following form: Imagine a right sixteen-sided prism, and in each angle 1 At. C, making in all 32 At. C; in the middle, between each two angles, 1 At. H, making together 32 At. H.; and lastly, on each base of the prism, 1 At. HO, forming pyramids. Thus the compound = $C^{32}H^{32}$,2HO. In the same manner as crystals

* The above observations respecting the difference of properties between the so-called anhydrous organic acids and the hydrated acids, apply with equal force to the so-called anhydrous inorganic acids. The compound SO^3, for example, is not an acid in the strict sense of the word, but is converted into an acid by the action of water; and the formula HO,$C^4H^3O^3$ for hydrated acetic acid is neither more nor less objectionable than the formula HO,SO^3 for oil of vitriol. In both cases, it is best to regard the anhydrous compound, not as an acid, but as a product of decomposition of an acid. (*Vid. Organic Acids.*) [W.]

may be cleft mechanically, and the primary nucleus separated from the secondary envelope, so likewise may a chemical separation be made. After the removal of the two pyramids HO, there remains the primitive form [the *Germ* or *Nucleus*]. Cl or O acting on this primitive form withdraws the H; the prism would then fall to pieces, if the atoms of H were not replaced by atoms of Cl or O. The HCl or HO may either pass off, or form pyramids on the prism, which, however, may be removed by chemical division, *e. g.*, by the action of potash, &c. Further than this, Laurent has, so far as my knowledge goes, made no attempt to assign definite figures to particular compounds. Gerhardt, who for the most part adopts the views of Laurent, has, nevertheless, considerably extended them.

a. Dumas' Theory of Substitution and of Types.

Substitution.—1. One constituent of an organic compound may be partially withdrawn, without the substitution of another in its place, the compound being thereby transformed into another belonging to a different type. (Indigo-white, $C^{16}H^6NO^2$, gives up 1 At. hydrogen to the oxygen of the air, and is thereby converted into indigo-blue.)

2. In most cases, however, the abstracted element is replaced by an equal number of atoms of the acting substance: a *substitution* is effected. Not only may hydrogen be replaced by substitution, but likewise oxygen, nitrogen, and all other elements, even carbon. (*J. pr. Chem.* 20, 281.) [The assertion that carbon may be removed by substitution must be emphatically contradicted.] In a similar manner also, the atoms of an element may be replaced by an equal number of atoms of a compound.

3. In other cases, again, the atoms of one substance are replaced by more than an equal number of atoms of another. Thus C^4H^4 is converted by excess of chlorine, aided by sunshine, into $C^4Cl^6 = C^4Cl^4 + Cl^2$.

[For further observations on substitution, *vid. Decomposition of Organic Compounds*, pp. 71—76.]

Types.—Compounds containing equal numbers of atoms in the same relative position, and possessing the same fundamental properties, belong to the same *Chemical Type*. Hence, in such substitutions as those described in (2), a compound is transformed into another of the same chemical type. For an organic compound may be compared to a building; if the spaces left by withdrawing the atoms of one substance are filled up by those of another, the building retains its form; in the contrary case, it loses its form or falls to pieces. To the same chemical type belong Acetic acid, $C^4H^4O^4$, and Chloracetic acid, $C^4HCl^3O^4$; further: Aldehyde, $C^4H^4O^2$, and Chloral, $C^4HCl^3O^2$ [and Chloraldehyde, $C^4Cl^4O^2$]; further: Chloroform, C^2HCl^3; Bromoform, C^2HBr^3; Iodoform, C^2HI^3; and Marsh-gas, C^2H^4; further: Olefiant gas, C^4H^4, and the products obtained therefrom by chlorine, viz. C^4H^3Cl; $C^4H^2Cl^2$; C^4HCl^3, and C^4Cl^4.

Compounds belonging to the same type exhibit their agreement in fundamental properties, principally by yielding analogous products of decomposition. Acetic acid, $C^4H^4O^4$, heated with excess of fixed alkali, is resolved into $2CO^2$ and marsh-gas C^2H^4; chloracetic acid, when merely boiled with excess of aqueous potash, likewise yields $2CO^2$, and chloroform, C^2HCl^3, which belongs to the same type as marsh-gas,—whence also, marsh-gas, when treated with chlorine, yields hydrochloric acid, and is converted, first into chloroform, and then into C^2Cl^4.

If two compounds, one of which can be formed from the other by

substitution, contain equal numbers of atoms similarly united, but are possessed of strikingly different chemical properties (one, for example, being acid, while the other is neutral or basic), they can no longer be regarded as belonging to the same chemical type, but may nevertheless be included in the same *mechanical* or *molecular type;* they therefore still constitute a natural family.—Thus: Wood-spirit, $C^2H^4O^2$, and formic acid, $C^2H^2O^4$; alcohol, $C^4H^6O^2$, and acetic acid, $C^4H^4O^4$; ether, C^4H^5O, and aldehyde, $C^4H^4O^2$, &c.

[Dumas' types form the members of which each particular series in Laurent's nucleus-theory is composed.]

¶ *Connection between the Radical-theory and the Theory of Types and Substitution.*

The doctrine of types and substitution has generally been regarded as opposed to the radical-theory, and was at first encountered with strong opposition by the chief supporters of the latter. In fact, most chemists who have adopted the radical-theory have used it strictly in the manner in which it was first proposed by Berzelius (vide p. 9), rejecting, or at least ignoring, the doctrine of chemical types. On the other hand, Laurent & Gerhardt, to whom we are indebted for the most complete development of the theory of types and substitution, have always been the most determined opponents of the radical-theory. Recent investigations, however, have shown that the idea of types is quite as consistent with the theory of radicals as with the nucleus-theory; and Gerhardt himself, in his recent paper "On the Constitution of Organic Acids," (*Chem. Soc. Qu. J.* 5, 127,) has adopted, without reservation, the formulæ of the radical-theory.

The connection between the radical and type theories is strikingly exhibited by the substitution of the alcohol-radicals, methyl, ethyl, &c., for hydrogen, in the compound ammonias discovered by Wurtz and Hofmann, and in the compound ethers discovered by Williamson.

1. In 1848, Wurtz discovered that when the cyanates of methyl, ethyl, and amyl are acted upon by caustic potash, volatile alkaline products are formed, strongly resembling ammonia in odour and other physical characters, but differing from it by containing the elements of methyl, ethyl, and amyl, in place of 1 atom of hydrogen: these bodies are respectively

$$\text{Methylamine} = \left\{\begin{matrix} H \\ H \\ C^2H^3 \end{matrix}\right\} N = C^2H^5N$$

$$\text{Ethylamine} = \left\{\begin{matrix} H \\ H \\ C^4H^5 \end{matrix}\right\} N = C^4H^7N$$

$$\text{Amylamine} = \left\{\begin{matrix} H \\ H \\ C^{10}H^{11} \end{matrix}\right\} N = C^{10}H^{13}N$$

More recently Hofmann has shown that, by the action of the bromides and iodides of the alcohol-radicals on ammonia and aniline (which may be regarded as *phenylamine* = $(H,H,C^{12}H^5)N$, one, two, three, and even four atoms of hydrogen may be replaced by the alcohol-radicals, the first three substitutions yielding volatile bases analogous to ammonia, and the fourth producing compound metals analogous to ammonium. These last-mentioned compounds, like ammonium itself, have not actually been

isolated; but in the state of hydrated oxides, they form solid compounds resembling the hydrates of potash and soda, and yield solutions having a strong alkaline and corrosive action, and capable of saponifying fats like the fixed alkalis. These several compounds, of which ammonia H^3N, and hydrated oxide of ammonium H^4NO,HO, are the types, may be represented by the following general formulæ, in which the letters V, X, Y, Z, denote the radicals ethyl, methyl, &c.

Amidogen-bases.	Imidogen-bases.	Nitrile-bases.
(H,H,X)N	(H,X,Y)N	(X,Y,Z)N

Bases analogous to Oxide of Ammonium.

(V,X,Y,Z)NO,HO

The following are a few examples:* Methylethylamine=(H,Me,Et)N; Diethylamine $(H,Et^2)N$; Methylophenylamine=(Me,Et,Ph)N; Diethylophenylamine $=(Et^2,Ph)N$; Triethylamine $=Et^3N$; Tetrethylium $=Et^4N$; Methylethylamylophenylium = (Me,Et,Am,Ph)N.

The view thus given of the constitution of these bases is perfectly consistent with the known analogies of chemical compounds. The alcohol-radicals are now proved, by the researches of Frankland and Kolbe, to be really existing substances; and we further know that they are analogous in many respects to hydrogen (*vid. Alcohol-radicals*). In accordance with this analogy, we find them taking the place of hydrogen in ammonia, and producing compounds which bear the strongest resemblance to that body in volatility, alkaline reaction, &c. The composition of these bases may, of course, be represented in various other ways (*vid. Alkaloids*); but the view just given affords at least a satisfactory account of their formation and properties, and may serve to show that the idea of radicals is by no means inconsistent with the doctrine of chemical types.

2. A further illustration of the connection between types and radicals may be found in the recent investigations of Williamson and Gerhardt.—Adopting Gerhardt's equivalents (page 27), we may consider water, H^2O, as the type of all the most important chemical compounds, alcohols, ethers, salts, acids, &c. The substitution of one atom of a metal for 1 at. hydrogen in this type, gives the hydrated oxide of that metal, and the replacement of both atoms of hydrogen by the metal forms the anhydrous oxide; *e. g.*, hydrate of potash $= \begin{matrix}K\\H\end{matrix}O$; anhydrous potash $= \begin{matrix}K\\K\end{matrix}O$. Similarly, an alcohol is water in which 1 At. H is replaced by a compound radical, such as methyl, ethyl, &c.; and an ether is water with both atoms of hydrogen thus replaced: thus, common alcohol $= \begin{matrix}C^2H^5\\H\end{matrix}O$; common ether $= \begin{matrix}C^2H^5\\C^2H^5\end{matrix}O$. The two atoms of hydrogen may also be replaced by different compound radicals, the products being the compound ethers discovered by Williamson, viz.

$$\begin{matrix}CH^3\\C^2H^5\end{matrix}O = C^3H^8O;\quad \begin{matrix}CH^3\\C^5H^{11}\end{matrix}O = C^6H^{14}O;\quad \begin{matrix}C^2H^5\\C^5H^{11}\end{matrix} = C^7H^{16}O.$$

The mode of formation of these last-mentioned compounds justifies the view here taken of the constitution of alcohols and ethers. When alcohol—which may be regarded as an acid (ethylic acid), containing 1 At. of basic hydrogen replaceable by a metal—is acted upon by potas-

* C^2H^3 = Me; C^4H^5 = Et; $C^{10}H^{11}$ = Am; $C^{12}H^5$ = Ph.

sium, 1 At. H escapes, and 1 At. K takes its place, yielding potassium-alcohol or ethylate of potassium $\begin{matrix}C^2H^5\\K\end{matrix}O$. Now when this compound is treated with iodide of methyl, CH^3I, the potassium of the one compound and the methyl of the other change places, and we get KI and $\begin{matrix}CH^3\\C^2H^5\end{matrix}O$. The other compound ethers are formed in a similar manner.

A like view may be given of the constitution of organic acids; thus the substitution of 1 At. benzoyl, C^7H^5O for H in the formula $\begin{matrix}H\\H\end{matrix}O$, gives hydrated benzoic acid $\left.\begin{matrix}C^7H^5O\\H\end{matrix}\right\}O = C^7H^6O^2$, and the substitution of 2 At. benzoyl gives anhydrous benzoic acid or benzoic anhydride, $\left.\begin{matrix}C^7H^5O\\C^7H^5O\end{matrix}\right\}O = C^{14}H^{10}O^3$, the compound which Gerhardt has lately obtained by the action of chloride of benzoyl on benzoate of soda (*vid. Organic acids*). [For further developments of these views, *vid. Chem. Soc. Qu. J.* 5, 350.]—To accommodate this theory to the atomic weights adopted in the present work, we must consider the several compounds as formed upon the type of 2 At. water, H^2O^2; *e. g.*, alcohol $= \begin{matrix}C^4H^5\\H\end{matrix}O^2$, ether $\begin{matrix}C^4H^5\\C^4H^5\end{matrix}O^2$, &c. ¶

b. Laurent's Nucleus-theory.

The atoms of organic compounds are either *Nuclei* (*Kerne, Noyaux*), or compounds of these nuclei with various substances attached to them externally. [Laurent frequently designates the nuclei by the term *Radicals;* but this appellation has a tendency to confound them with the radicals of the above-mentioned *radical-theory*, from which, in reality, they differ very materially. The former contain even, the latter uneven numbers of atoms.]

The number of carbon-atoms in the nucleus is always even; so likewise is that of the other atoms, and consequently of the whole collection of atoms composing the nucleus. [Such is the law according to the atomic weights adopted in this Hand-book; but as Laurent makes the atomic weights of carbon and hydrogen only half as great, the number of atoms of each of these elements in the nucleus must, according to his theory, be divisible by 4.]

The number of carbon-atoms in the nucleus bears a simple relation to that of the other atoms; *e. g.*, 2:2; 4:4; 8:8; 32:32; 6:4; 12:6; 12:8; 14:6; 18:8, &c. Less simple relations are of rare occurrence.

If the nuclei contain nothing but hydrogen in addition to the carbon, they are called *Primary Nuclei* (*Stammkerne, Noyaux fondamentaux, Radicaux fondamentaux*).—But if one, or several, or all of the hydrogen-atoms of the nucleus are replaced by atoms of other elements, or of certain compounds, organic or inorganic, which take the same place in the nucleus that the hydrogen-atoms originally occupied, the compound atoms thus formed are called *Derivative* or *Secondary Nuclei* (*abgeleitete Kerne, Noyaux derivés, Radicaux derivés*). Hence, in the theory of nuclei, less importance is attached to the nature of the elements than in the radical-theory, and more to their configuration.

The elements which usually replace the hydrogen in the nucleus are I, Br, Cl, O, N, and the metals. (With regard to nitrogen, it must be observed, that Laurent assigns to it two different atomic weights; Az, in Laurent's system $= \frac{1}{2}$ N of this Hand-book $= 7$; and N in Laurent's system $= \frac{1}{8}$ N of this Hand-book $= \frac{14}{3}$).

When the hydrogen of a nucleus is replaced by a compound, each

atom of hydrogen is replaced by one atom of the compound. [It need not excite astonishment, that the space originally occupied by 1 At. hydrogen may afford room, not only for an atom of chlorine, the weight of which is 36 times as great, but even for the 5 atoms of hyponitric acid, NO^4, whose weight is 46 times as great as that of the hydrogen: for in no compound are the atoms in immediate contact. Affinity, indeed, strives to bring them together as closely as possible; but the elasticity of the heat-sphere surrounding each of them produces the contrary effect; and, the two forces balancing one another, each atom remains separated from the next, by a distance many times greater than the diameter of a single atom. Consequently, a space occupied by one atom of hydrogen, with its heat-sphere, may subsequently afford room for several atoms of other substances; the heat-spheres of the latter must, however, take up less space than that of the hydrogen-atom.]

The compounds capable of replacing hydrogen in the nucleus, are: NO^4, which, for shortness, may be expressed by the symbol X; N^4H^4 = Im = Imidogen; NH^3 = Ad = Amidogen; NH^3 = Am = Ammonia; AsH^2 = Ar = Arsidogen; C^2N = Cy = Cyanogen, &c. [The assumption of imidogen $= N^4H^4$, is admissible only when (according to the system of Berzelius and Laurent) we suppose the atom of hydrogen = 0·5, and that of nitrogen = 7 (O = 8); according to the atomic weights of this Hand-book, on the contrary, this supposition is inadmissible, on account of the fractions which it introduces. It is, moreover, unnecessary, inasmuch as we do not know with certainty of any compound containing only 1 atom of imidogen; and in those cases where Laurent supposes $2Im (= 2 . N^4H^4)$, we may just as well write NH.]

When, by the action of various substances, one nucleus is converted into another, without loss of carbon, the new compound cannot be represented by a formula, in which the nucleus is supposed to contain a number of carbon-atoms different from the former. When, on the contrary, a portion of the carbon separates from the nucleus, in the form of carbonic acid for example, the old nucleus must be replaced by another containing a smaller number of carbon-atoms, and therefore standing lower in the organic scale,—or a compound of such a nucleus with certain substances superadded. When decomposition takes place in such a manner, that the hydrogen, &c., withdrawn from the nucleus is replaced by an equal number of atoms of chlorine, &c., the nucleus remains the same, but is transformed more or less into a secondary nucleus. When, however, hydrogen, chlorine, &c., is withdrawn without substitution, the residue, if still an organic compound, must belong to the series of another nucleus. The replacement of a certain number of atoms of hydrogen in the nucleus by chlorine, bromine, or iodine, does not alter the properties of a compound so much as the replacement of an equal number of atoms of hydrogen by O, NO^4, or NH^2. Moreover, all nuclei are neutral, even when they contain O, Cl, Br, NO^4, &c.

Examples of Nuclei: In the Ethene-series, Olefiant gas = C^4H^4 = *Ethène*, the *primary nucleus*. — Secondary nuclei are: *Chlor-ethase* = C^4H^3Cl; *Brom-ethase* = C^4H^3Br; *Ar-ethase* = C^4H^3As [this nucleus is supposed by Laurent to exist in cacodyl = C^4H^6Ar; this compound, assuming $Ar = AsH^2$, he writes = C^4H^3Ar,H]; *Chlor-ethèse* = $C^4H^2Cl^2$; *Chlor-ethise* = C^4HCl^3; *Chlor-ethose* = C^4Cl^4.

The termination *se* denotes a secondary nucleus, the vowel before the *se* indicating the number of hydrogen-atoms which are replaced by another substance. When 1 At. H is replaced, the name of the resulting com-

pound ends in *ase;* *ese* indicates 2 At. of hydrogen replaced, *ise* 3, *ose* 4, *use* 5; *alase* 6, *alese* 7, *alise* 8. If the element which replaces the hydrogen is not specially named, it is tacitly understood to be oxygen. When any other element takes the place of the hydrogen, its name is prefixed. Thus, chlorethase is ethene in which 1H is replaced by 1Cl; and in chlorethose, all 4 atoms of hydrogen are replaced by 4 At. Cl.

In the *Naphthene-series*, Napthaline=*Naphthene*=$C^{20}H^8$, is the *primary nucleus;* the following are some of the 33 secondary nuclei derived from it: *Naphthase*=$C^{20}H^7O$; *Chlonaphthase*=$C^{20}H^7Cl$; *Ninaphthase*= =$C^{20}H^7X$; *Amanaphthase*=$C^{20}H^7Ad$; *Bronaphthese*=$C^{20}H^6Br^2$; *Chloranaphthese*=$C^{20}H^6OCl$; *Chlonaphthise*=$C^{20}H^5Cl^3$; *Aminaphthise*=$C^{20}H^5Ad^3$; *Bronaphthose*=$C^{20}H^4Br^4$; *Chlorénaphthose*=$C^{20}H^4Cl^2O^2$; *Chlorébronaphthose*=$C^{20}H^4Br^2Cl^2$; *Chloribronaphthose*=$C^{20}H^4BrCl^3$; *Chloréninaphthose* =$C^{20}H^4XCl^3$; *Chloribronaphthuse*=$C^{20}H^3Br^2Cl^3$; *Chlonaphthalase*= $C^{20}H^2Cl^6$; *Chloroxénaphthalese*=$C^{20}HCl^5O^2$; *Chlonaphthalise*=$C^{20}Cl^8$.

All these secondary nuclei belong to the same series as the primary nucleus. They have all the same type,—that is to say, they all contain the same number of carbon-atoms with the same number of atoms of other atoms similarly annexed to them and forming similar geometrical figures.

But inasmuch as the atoms of different elements are frequently attached externally to the nucleus, several new types are produced, belonging to the same series, but differing from one another according to the number and nature of the externally annexed atoms. The number of the atoms thus externally attached is, with very few exceptions, 2, 4, or 6, rarely more.

Hydrogen is rarely attached to the nucleus, and only to the amount of 2 atoms; thus, Marsh-gas, C^2H^4, may be regarded as C^2H^2 (Methylene) + H^2. By supposing 1 At. H to be combined with a primary nucleus, we may explain the formation of many of the radicals in the binary theory (*e. g.*, Methyl=C^2H^2+H), which may be regarded as organic metals or *fundamental Metalloids* (*Prométallides fondamentaux*), but are nearly all merely hypothetical. (*Vid.* Note, p. 12.)

With regard to the combinations of nuclei with *Chlorine*, *Bromine*, *Oxygen*, &c., two suppositions may be made. Formerly, Laurent maintained that chlorine or oxygen cannot unite with a primary nucleus as such; but that this nucleus must be converted into a secondary nucleus by the substitution of chlorine or oxygen for part of its hydrogen, before it can take up Cl, O, HCl, or HO, externally to itself.

When, for example, olefiant gas=ethylene=C^4H^4, combines with 2Cl, it forms the oil of olefiant gas=$C^4H^4Cl^2$; this oil may be regarded either as C^4H^3Cl,HCl, according to Laurent's earlier view, or according to that which he now adopts, as C^4H^4,Cl^2. Similarly, the compound of naphthaline with 2Cl may be expressed either by $C^{20}H^7Cl$,HCl, or by $C^{20}H^8$,Cl^2. The former view is supported by the fact that these compounds, when heated or subjected to the action of potash, give off, not Cl^2 but HCl, and are converted into the secondary nuclei, C^4H^3Cl and $C^{20}H^7Cl$.—In that case, however, the naphthaline-compound whose empirical formula is $C^{20}H^6Cl^2Br^4$ must be regarded as $C^{20}H^4Cl^2Br^2$,2HBr (not as $C^{20}H^6Cl^2$,Br^4). But this compound, when heated to 150° gives off, not 2HBr but 4Br; hence, according to the older view, it would be necessary to suppose that the 2H external to the nucleus, entered into it again and set free 2Br therefrom. (*Comp.* Laurent, *Rev. scientif.* 14, 74.) [Perhaps this singular

case may be explained by the affinity of the chlorine contained in the nucleus for hydrogen.]

Similarly, with regard to oxygen, Laurent maintained (*Ann. Chim. Phys.* 63, 218) that no primary nucleus can combine with oxygen and form an acid, unless part of its hydrogen has been previously replaced by another element, inasmuch as it has not yet been found possible, either to add oxygen to a primary nucleus without at the same time removing hydrogen, or to withdraw oxygen from an organic acid in such a manner as to leave the primary nucleus.

More recently, however (*Compt. rend.* 16, 856), Laurent controverts this view, because the reactions of the chlorine and bromine-compounds of napthaline (*vid. sup.*) render it probable that these compounds should be regarded as $C^{20}H^{8},Cl^{2}$ and $C^{20}H^{8},Br^{2}$, and not as $C^{20}H^{7}Cl,HCl$, or $C^{20}H^{7}Br,HBr$. Bitter almond oil, which, according to the older theory, $=C^{14}H^{6}O,HO$, and according to the more recent theory $=C^{14}H^{6},O^{2}$, is converted, by the action of hydrosulphate of ammonia, which takes away all the oxygen from 2 atoms of the oil, into Stilbene$=C^{28}H^{12}$, a transformation not so easily explained, if, according to the older theory, we suppose bitter almond oil to contain the secondary nucleus, $C^{14}H^{6}O$.

[The older theory is supported by the consideration that the primary nucleus, by the partial substitution of its hydrogen by another element, is brought out, as it were, from its former state of indifference and rendered more or less polar; the same theory, moreover, explains more clearly how it is that, in acids, a certain portion of the hydrogen (that, namely, which is external to the nucleus) may be replaced by metals, while the remaining portion (forming part of the nucleus) is incapable of this kind of substitution, but may nevertheless be replaced by chlorine, &c. The later theory, on the other hand, has the advantage of yielding much simpler formulæ.]

Chlorine, Bromine, Iodine, or *Sulphur*, may combine with the nucleus to the number of 2—6 atoms. Either of these elements may be removed by potash, without the substitution of another substance;—in such a case, either the whole of the chlorine or bromine passes over to the potash, externally to the nucleus, the latter being left in its original state, or half the external atoms, together with an equal number of hydrogen-atoms, are taken up by the potash, while the other half of the chlorine or bromine-atoms pass over to the nucleus to replace the hydrogen-atoms. But the chlorine or bromine belonging to the nucleus is not easily removed by potash; and when it is thus withdrawn, and not replaced by any other substance, the nucleus is either transformed into another, or completely decomposed.

The following compounds, belonging to the ethene-series, afford examples of these transformations: Oil of olefiant gas$=$*Chloride of Ethene*$=C^{4}H^{4},Cl^{2}$; similarly $C^{4}H^{4},Br^{2}$; $C^{4}H^{4},I^{2}$; *Chloride of Chlorethase* $=C^{4}H^{3}Cl,Cl^{2}$; *Chloride of Chlorethise*$=C^{4}HCl^{3},Cl^{2}$; Sesquichloride of Carbon$=$*Chloride of Chlorethose*$=C^{4}Cl^{4}Cl^{2}$, &c.

A nucleus, either primary or secondary, may take up, externally, 2, 4, or 6 atoms of *Oxygen*.

By taking up 2 atoms of oxygen it is generally converted into a *neutral oxide*, rarely into a *slightly acid compound*. The product is a *fundamental* or *derived Protogenide* (*Protogénide fondamental ou derivé*), according as the nucleus which takes up the 2O is primary or secondary.

Examples of neutral oxides: Aldehyde, C^4H^4,O^2; Bitter almond oil, $C^{14}H^6,O^2$; *Oxide of Chloroxénaphthalise*, $C^{20}Cl^6O^2,O^2$.—The following are weak acids: Phenic acid, $C^{12}H^6,O^2$; Bromophenassic acid, $C^{12}H^5Br,O^2$; Chlorophenassic acid, $C^{12}HCl^5,O^2$; Picric or Nitrophenissic acid, $C^{12}H^3X^3,O^2$; Salicylous acid, $C^{14}H^6O^2,O^2$.

The addition of 4 atoms of oxygen to the nucleus produces a *Monobasic acid* (*Sel monobasique*). [Since the only difference between an acid and its salts is that the former contains an atom of hydrogen where the latter contain an atom of metal, it is evident that the acid itself may likewise be regarded as a salt.]—By this change, 1 At. H must be rendered capable of interchanging with 1 At. metal.

The following are monobasic acids: Formic acid, C^2H^2,O^4 (its metallic salts, C^2HM,O^4); Acetic acid, C^4H^4,O^4 (metallic salts, C^4H^3M,O^4); Butyric acid, C^8O^8,O^4 (metallic salts, C^8H^7M,O^4); Benzoic acid, $C^{14}H^6O^4$ (metallic salts, $C^{14}H^5M,O^4$); Salicylic acid, $C^{14}H^6O^2,O^4$ (metallic salts, $C^{14}H^5MO^2,O^4$). In benzoic acid, the primary nucleus is C^4H^6=Benzene; in salicylic acid, it is $C^{14}H^8$=Salene.

The addition of 6 At. oxygen to a nucleus produces a *Bibasic acid* (*Sel bibasique*).—In this case, 2 atoms of hydrogen must be brought into such a state as to be replaceable by 2 atoms of a metal.—The following are examples of bibasic acids with their metallic salts: Oxalic acid, $C^4H^2O^2,O^6$ ($C^4M^2O^2O^6$; the primary nucleus is Ethene=C^4H^4); Phthalic acid, $C^{16}H^6O^2O^6$ ($C^{14}H^4M^2O^2,O^6$; the primary nucleus is Phthalene=$C^{14}H^8$).

Those acids which are more than bibasic, are regarded by Laurent (some of them, at least) as intimate compounds of several simple acids.

Two atoms of hydrogen and 2 atoms of oxygen may likewise be attached to the nucleus, not exactly in the form of 2 At. HO, but in some other form. In this manner are produced the Alcohols, in the wider sense of the term.—With regard to the alcohol of the ethene series, viz. common alcohol, $C^4H^6O^2$, Laurent's view accords very nearly with the radical-theory: Ethene, C^4H^4, is converted by addition of hydrogen into the metalloid, Ethyl=C^4H^4,H; this, by addition of O becomes Oxide of Ethyl; and by further addition of 1 At. oxide of hydrogen, Alcohol=$C^4H^4H,O+HO$, is produced. Similarly with wood-spirit, &c. But the alcohols may, after all, have a totally different constitution, and may not contain either a metalloidal radical, or 1 At. water ready formed. We may suppose, indeed, that several atoms of H and O are annexed externally to the nucleus, without being actually united in the form of water.

When oxygen or chlorine accumulates outside the nucleus in too great quantity, the nucleus is apt to resolve itself into two other nuclei, containing only half as many carbon-atoms, and therefore belonging to a lower series. In this manner, Chloral=C^4HCl^3,O^2, which belongs to the ethene-series, is resolved, by the action of aqueous alkalis, assisted by 2HO, into formic acid=C^2H^2,O^4, and chloroform=C^2HCl^3,—both of which belong to the methylene-series.

Most nuclei, both primary and secondary, which occur in other types, as in acids, &c., are likewise known in the separate state; but the existence of many primary nuclei is merely hypothetically assumed from that of their derived nuclei; many nuclei also, both primary and secondary, are merely supposed to exist, because the composition of a certain series of compounds is best understood by regarding them as composed of an unknown nucleus combined with other substances. Thus, the exist-

ence of Methylene or Palene, C^2H^2, is not yet satisfactorily demonstrated; but it is assumed, because many compounds, viz., Marsh-gas $= C^2H^2,H^2$; Formic acid $= C^2H^2,O^4$; Methylic ether $= C^2H^2,HO$; Wood-spirit $= C^2H^2,H^2O^2$, &c., are most conveniently derived from that substance as a nucleus.

Compounds belonging to the same type of the same series have a certain physical and chemical similarity (and are likewise isomorphous), even if the nucleus of the one contains nothing but hydrogen besides the carbon, while that of the other contains more or less chlorine.—The four compounds of the phenene-series, $C^{12}H^6,O^2$; $C^{12}H^4Cl^2,O^2$; $C^{12}H^2Cl^4,O^2$; and $C^{12}HCl^5,O^2$, for example, all fuse very readily, volatilize without decomposition, are scarcely soluble in water, but dissolve with facility in alcohol and ether. But compounds of the same series, which belong to different types, exhibit marked differences in their properties, even when they differ but slightly in the numbers of atoms of which they are made up: *e.g.*, Indigo-blue $= C^{16}H^5NO^2$, and Indigo-white $= C^{16}H^6NO^2,H$.

Laurent's Classification.

Organic compounds may be arranged in *series*. The basis of each of these series is a primary nucleus, together with its secondary nuclei. Thus, the following compounds belong to the series of Ethene or Ethylene, C^4H^4; Aldehyde, C^4H^4,O^2; Alcohol, C^4H^4,H^2O^2; Acetic acid, C^4H^4,O^4; Choracetic acid, C^4HCl^3,O^4, &c.

Each series contains compounds belonging to different types, and these types reappear in other series. Thus the nucleus-type includes all nuclei, primary and secondary; the alcohol-type, all nuclei to which H^2O^2 has been added; the monobasic acid type, all nuclei which have taken up 4O in addition, &c.

A primary nucleus may be altered by abstraction of 2H; the remainder is the *Characteristic*, which, in the case of methylene, C^2H^2, is merely C^2, while in other nuclei it is C^2 + the remainder of the hydrogen. The 2H are the *Constant;* so that every primary nucleus = Car. + Const. = Car, H^2. Hence the compounds of any series may be arranged and designated as follows:—

A. *Nuclei.*

a. *Ethénides = Primary Nuclei* = Car, H^2.

The conjugated acids, which these primary nuclei form with sulphuric acid, &c., are called by Laurent, *Sels non métaleptiques*, because in the nucleus, no substitution (*metalepsie*) of hydrogen by another substance has taken place.

b. *Ammonides.* 1H of the constant is replaced by amidogen, NH^2.

a. Amm. actifs = Car, HAd. The characteristic remains unaltered. With acids, they form compounds called *Sels métaleptiques.*

β. Amm. passifs = Car, $-xH+xCl$,HAd. Part of the hydrogen in the characteristic is replaced by chlorine or some other salt-radical..

c. *Analcides.* The hydrogen of the constant, and partly also in the characteristic, is replaced by a salt-radical, by hyponitric acid or by oxygen.

a. Halydes = Car $-xH+xCl,Cl^2$.—All the hydrogen of the constant, and part of that in the characteristic is replaced by chlorine, bromine, or iodine. These nuclei are not decomposed by alkalis.

β. Nitrides = Car, HX. Take fire when heated in close vessels, are

decomposed by potash, and converted into *Ammonides* by hydrosulphuric acid.

γ. *Camphides* = Car, O^2. Little known. Common camphor, $C^{20}H^{16},O^2$, may be regarded as one of them.

B. *Protogénides.* Compounds of nuclei with 2 At. hydrogen or oxygen, or with 2, 4, or 6 atoms of a salt-radical.

a. *Hydrides* = Car, $H^2 + H^2$. Marsh-gas, $C^2H^4 = C^2H^2 + H^2$, is the hydride of palene or methylene, C^2H^2.

b. *Hyperhalydes* = Car, $H^2 + Cl^2$ (or Cl^4 or Cl^6); or likewise $Car - H^x + Cl^x, Cl^2 + Cl^2$ (or Cl^4 or Cl^6). Bromine or iodine may likewise enter in place of chlorine. This addition of 2 or 4Cl makes but little alteration in the characters of these compounds. Alkalis remove from them the chlorine which is external to the nucleus, and leave the latter in the free state. To this class belong, for example: $C^2,H^2 + Cl^2$; $C^2,Cl^2 + Cl^2$; $C^4H^2,H^2 + Cl^2$; $C^4Cl^2,Cl^2 + Cl^2$; $C^8H^6,H^2 + Cl^2$; $C^{10}H^8,H^2 + Cl^2$; $C^{12}H^4,H^2 + Cl^6$; $C^{14}H^6,Cl^2 + Cl^2$; $C^{14}H^6,Cl^2 + Cl^6$; $C^{20}H^{16},O^2 + Br^2$; $C^{20}H^6,Cl^2 + Cl^2$; $C^{20}H^4Cl^2, Cl^2 + Cl^4$. The substances before the comma form the characteristic; those after the comma, the constant; those after the + sign are the substances external to the nucleus.

c. *Anhydrides.* [As Laurent gives the name *Anhydrides* to compounds which are also destitute of water, he ought to have designated his *Hydrides*, *i. e.*, compounds of the nuclei with hydrogen, by some other term.]—Compounds of secondary nuclei with Cl^2, Cl^4, Cl^6, or O^2, which, when subjected to the action of aqueous alkalis, take up the elements of 2 or 4HO, and are thereby converted into acids or ammoniacal salts.

α. *Haloformes* = Car, $HCl + Cl^2$, Cl^4 or Cl^6 (or Br or S instead of Cl). Aqueous alkalis convert these compounds into monobasic acids. Chloroform, $C^2,HCl + Cl^2$ with 4HO forms $3HCl + C^2H^2O^4$ (formic acid). To the same division belongs: $C^4H^2,HCl + Cl^2$. [According to this, the hyperhalydes are identical with the haloform anhydrides, so far as their constitution is concerned, and differ only in their behaviour with aqueous alkalis.]

β. *Anhydrhalydes* = Car, $Cl^2 + O^2$. To this division belong $C^{20}H^4O^2,Cl^2 + O^2$, and chloraldehyde, $C^4Cl^2,Cl^2 + O^2$. The latter is converted by the action of aqueous potash into hydrochloric and chloracetic acids.

$$(C^4Cl^2,Cl^2 + O^2) + 2HO = HCl + (C^4Cl^2,HCl + O^4).$$

γ. *Amides* = Car, $HAd + O^2$. These compounds, when decomposed by aqueous alkalis, yield 1 At. ammonia and 1 At. monobasic acid: Benzamide = $C^{14}H^4,HAd + O^2$, yields, with 2HO; $NH^3 + C^{14}H^4,H^2 + O^4$. In a similar manner, salicylamide yields salicylic acid:

$$C^{14}H^4O^2,HAd + O^2 + 2HO = NH^3 + C^{14}H^6,O^2 + O^4.$$

δ. *Anhydracides* = Car, $O^2 + O^2$. Form bibasic acids by taking up 2HO. When succinic acid, $C^8H^6O^2 + O^6$, is distilled with anhydrous phosphoric acid 2HO, is taken away, and the anhydracid, $C^8H^4O^2,O^2 + O^2$ is obtained; and this, by contact with 2HO is restored to the state of succinic acid. Chloranil is resolved, by contact with aqueous potash, into hydrochloric and chloranilic acids:—

$$(Cl^{12}Cl^4,O^2 + O^2) + 4HO = 2HCl + (C^{12}H^2Cl^2,O^2 + O^6).$$

ε. *Biamides* = Car, $Ad^2 + O^2$. In contact with aqueous alkalis, they take up 4HO, and are converted into 2 At. ammonia and 1 At. bibasic acid.

$$\underbrace{C^8H^4O^3,Ad^2 + O^2}_{\text{Succinamide.}} + 4HO = 2NH^3 + \underbrace{C^8H^6,O^2 + O^6}_{\text{Succinic acid.}}$$

$$\underbrace{C^4O^2,Ad^2 + O^2}_{\text{Oxamide.}} + 4HO = 2NH^3 + \underbrace{C^4H^2,O^2 + O}_{\text{Oxalic acid.}}$$

ζ. *Biimides*=Car, Im^2+O^2. These compounds when treated with aqueous alkalis, yield 1 At. ammonia and 1 At. of a bibasic acid, Succinimide (the Bisuccinamide of other chemists)=$(C^8H^4O^3,Im^2+O^2)+4HO=NH^3+C^8H^6,O^2+O^6$ (succinic acid).—[If, according to the principles of this Hand-book, imidogen = N^1H^1, be regarded as inadmissible, the above formula of succinimide must be converted into C^8H^6N,O^2+O^2, or into $C^8H^3AdO^2,O^2$; and similarly with the other biimides.

d. *Aldehydes.* Compounds of the primary or secondary nucleus with 2O. By taking up 2O, they are converted into acids. [They evidently belong to the protogenides, under which division, also, many compounds of a secondary nucleus with 2O (or 2S) may be ranged, *e. g.*, the Anhydracids, Amides, Biamides, and Biimides].

These aldehydes may be subdivided into *neutral aldehydes* (Ethene-aldehyde=C^4H^2,H^2+O^2; Bitter almond oil=Benzene-aldehyde=$C^{14}H^4,H^2+O^2$; Sulphide of Benzene, $C^{14}H^4,H^2+S^2$);—*acid aldehydes* (Phenic acid $=C^{12}H^4,H^2=O^2$); and *derived aldehydes, i. e.*, containing a derived or secondary nucleus, and generally having an acid constitution (Chloral $=C^4HCl,Cl^2+O^2$; Chlorophenissic acid=$C^{12}H^3Cl,Cl^2+O^2$; Picric acid=$C^{12}H^3X,X^2+O^2$).

C. *Sels monobasiques*=Car, H^2+O^4. Monobasic acids, in which 1H of the constant may be replaced by a metal, yielding the formula: Car, $HM+O^4$.

a. *Sels monobasiques fondamentaux*=Car, H^2+O^4. Acetic acid=C^4H^2,H^2+O^4; a metallic acetate=$C^4H^2,HM+O^4$.

b. *Sels monobasiques derivés*=Car, $HCl+O^4$. Instead of HCl, the compound may contain HX. Chloracetic acid=$C^4Cl^2,ClH+O^4$; the metallic salt=$C^4Cl^2,ClM+O^4$.

c. *Sels monobasiques amidés*=Car, $AdH+O^4$. Several of these compounds are resolved, by the action of aqueous acids or alkalis, into ammonia and a bibasic salt [bibasic acid]; Oxamic acid=$C^4O^2,AdH+O^4$; the metallic salt, $C^4O^2,AdM+O^4$.

D. *Sels bibasiques.*—a. *Fondamentaux.* Compounds of a nucleus (containing O together with the H) with 6O; they contain 2 At. hydrogen, which may be replaced by a metal. Oxalic acid=C^4O^2,H^2+O^6; its metallic salts=C^4O^2,M^2+O^6; Succinic acid=$C^8H^4O^2,H^2+O^6$; its metallic salts=$C^8H^4O^2,M^2+O^6$.

b. *Derivés.* The nucleus combined with 6O contains Cl or NO^4.—Nitronaphthalic acid=$C^{16}H^3XO^2,H^2+O^6$; its silver-salt=$C^{16}H^3XO^2,Ag^2+O^6$.

c. *Viniques.* One atom of hydrogen in the constant is replaced by the organic metal, Ethyl=C^4H^5=E; and only the other can be replaced by a metal properly so called; Oxalovinic acid = $C^4O^2,EH+O^6$; its metallic salts=$C^4O^2,EM+O^6$.

E. *Prométallides.* Compounds of the nucleus with 1 At. H. Most of them are unknown in the separate state, but their existence may be hypothetically assumed. They coincide with the hypothetical radicals of the radical-theory.

a. *Fondamentaux.* Containing the primary nucleus; *e. g.*, C^4H^4+H.
b. *Dérivés, e.g.*, Cacodyle$=C^4H^3Ar+H$. ($Ar=AsH^2$.)
c. *Amidés.* Contain Ad.

F. *Syndesmides.* Formed by the union of two types, either from the same series$=$*Homodesmides*, or from different series$=$*Hétérodesmides*. They may be divided into *Anhydrides, Aldehydes, Salts,* &c. Thus Benzoin$=C^{28}H^{12}O^4$, formed, as it were, by the union of 2 atoms of bitter almond oil, $C^{14}H^6O^2$, is a homodesmide; and Mandelic acid, $C^{16}H^8O^6$, which may be regarded as a compound of bitter almond oil, $C^{14}H^6O^2$, with formic acid, $C^2H^2O^4$, is a heterodesmide.

I have considered it my duty thus to explain the more important doctrines of Laurent's theory, more especially as this theory has not yet received, at least in Germany, the attention which it deserves. Whoever will submit it to the test of examination, even if he does not agree with it in all its details, will nevertheless admit that the nucleus-theory is the one which affords the most simple and comprehensive view of the many thousands of known organic compounds, and unites them in the most natural families or series. With my own ideas this theory is in peculiarly close accordance, inasmuch as the view which it gives respecting the metallic salts of organic acids, is identical with that which I had proposed as the most probable, in the third edition of this work published in 1829 (Vol. 2); this will appear from the following quotations: Page 19. "According to the first view [that an organic compound when dried *per se* contains no more water], it must be admitted that the water which is disengaged in the combination of oxide of lead, or any other salifiable metallic oxide, with the organic substance, is not an educt, but a product formed by the union of all the oxygen in the metallic oxide with all or part of the hydrogen in the organic substance; and the residue thus obtained is not a compound of lead-oxide with a perfectly dehydrated organic substance, but a body distinguished from the organic substance perfectly dried *per se*, by the substitution of one equivalent of lead or another metal for one equivalent of hydrogen. Hence, according to the first view, to which the preference is given in the course of this work, an organic substance dried as far as possible *per se* must be regarded as *perfectly anhydrous;* and the hypothetical organic compound of a still greater degree of dryness, which, according to the second view, is supposed to combine with the oxide of lead, but can never be obtained in the separate state, must be distinguished from the former by the appellation of a *hypothetically anhydrous* organic compound. The former view corresponds to the chloristic, the latter to the antichloristic theory, as may be seen by substituting hydrochloric acid gas for the organic compound. According to the first view, the water produced in the act of combination with metallic oxides is a product, and the metal combines with the chlorine in the one case, and with the organic compound freed from one atom of water in the other. According to the latter view [which supposes that water, previously in a state of intimate combination, is expelled by the metallic oxide], the water is an educt, and the metallic oxide combines with the hypothetically anhydrous muriatic acid or with the hypothetically anhydrous organic compound."

Further, pp. 28–29. "Many neutral oxalates of metallic oxides, when heated above 100°, are resolved into water and a compound of 2 equivalents of carbon with 4 oxygen and 1 metal, which may be called a metallo-oxalic acid (*e. g.*, plumbo-oxalic acid), inasmuch as in this compound the 1 equivalent of hydrogen is replaced by 1 equivalent of the metal; or we may regard it, with Dulong, as a compound of 2 eq. of carbonic acid with 1 eq. of the metal," &c.

Further, p. 316. (With regard to the ethers formed from alcohol by the action of hydrogen-acids.) "(1.) They are either ternary compounds, viz., ether in which 1 eq. of oxygen is replaced by 1 eq. of another electro-negative substance (iodine, bromine, or chlorine)," &c.—The preference is given to this view.

Finally, pp. 324–325. (With regard to the ethers formed from alcohol by oxygen-acids.) "They may either be regarded as formed by the direct combination of the

elements of the ether with those of the acid into a whole, in which the acid is no longer present, and consequently no longer exhibits its ordinary reactions," &c.

Dulong, *Mém. de la Classe des Sc. math. et phys. de l'Institut.* 1813, 1814 and 1815, p. cxcix) was the first to show that anhydrous oxalic acid and the hypothetically anhydrous oxalate of lead might be regarded as compounds of 2 At. carbonic acid with 1 At. hydrogen or lead, &c. *Comp.* also Murray (*Ann. Phil.* 11, 281); Thomson (*Ann. Phil.* 18, 146).

c. Gerhardt's Equivalents.

At the time when the doctrine of affinity in this Hand-book was written, Gerhardt's late attempt at determining the atomic weights of bodies had not appeared. Now, as the knowledge of these determinations is necessary to the understanding of the formulæ of organic compounds hereafter to be given, and as they have likewise some influence on the mode in which many transformations of organic compounds are to be understood, the present appears to be the most proper place for introducing them. Several other of Gerhardt's views relating to the nucleus-theory, will be explained in speaking of substitution, conjugated acids, amidogen-compounds, &c.

According to Gerhardt, the atomic weights and equivalents of the elements and their compounds, had not been correctly determined, for want of due attention to the volume-relations of the elements and their compounds in the gaseous state.

We must suppose, with Berzelius, that equal volumes of the simple gases contain equal numbers of atoms, and therefore, since 2 vol. hydrogen combine with 1 vol. oxygen to form water, that 1 At. water contains 2 At. hydrogen and 1 At. oxygen; and accordingly if 1 At. oxygen weighs 100 (8), 1 At. hydrogen must weigh 6·28 (0·5). [*Comp.* I. 45.] For similar reasons, the equivalents of iodine, bromine, chlorine, fluorine, and nitrogen, must, as in the system of Berzelius, be taken at half the values assigned to them in this work. Moreover, according to Gerhardt, this halving of the equivalents must also be extended to most of the metals. For mercuric oxide contains 8 pts. oxygen to 100 pts. mercury, and the vapour-density of mercury is to that of oxygen nearly as 6·9 : 1·1; hence, for the formation of mercuric oxide, 2 vol. vapour of mercury and 1 vol. oxygen gas are required; for $2 \cdot 6{\cdot}9 : 1{\cdot}1 = 100 : 8$ (nearly). According to this, the equivalent of mercury (that of oxygen being 8) is equal to 50, and the formula of mercuric oxide is Hg^2O (that of mercurous oxide $= Hg^4O$). Now, since the chemical relations of mercuric oxide are analogous to those of cupric oxide, ferrous oxide, zinc-oxide, manganous oxide, magnesia, lime, potash, &c., it follows that these latter are not composed of CuO, FeO, ZnO, MnO, MgO, CaO, KO, &c., but of Cu^2O, Fe^2O, Zn^2O, Mn^2O, Mg^2O, Ca^2O, K^2O, &c., their formulæ are thus brought into accordance with that of water, H^2O, and the equivalents of these metals, compared with that of oxygen, are reduced one-half.

We may, however, proceed in two ways, viz. (*a*), leave the equivalents of O, C, S, Se, as they are given in this Hand-book, and halve those of H, I, Br, Cl, F, N, and the metals; or (*b*), leave the latter equivalents as they are given in the present work, and double those of O, C, S, and Se: in either case we obtain Gerhardt's equivalents. In the following table, which includes the elements of most frequent occurrence in organic

compounds, the atomic numbers, as given in this Hand-book, are placed for comparison, beneath those of Gerhardt.

	O	C	S	Se	H	P	I	Br	Cl	N	K	As
According to (*a*)	8	6	16	40	0·5	15·7	63	39·2	17·7	7	19·6	37·5
According to (*b*)	16	12	32	80	1	31·4	126	78·4	35·4	14	39·2	75
Hand-book.....	8	6	16	80	1	31·4	126	78·4	35·4	14	39·2	75

To reduce Gerhardt's formulæ to those of the Hand-book, we have only to compare the equivalents of the series (*b*) with those of the Hand-book. The figures which in Gerhardt's formulæ, express the numbers of atoms of hydrogen, and the elements following it in the series, must be left unaltered, and those which relate to O, C, S, and Se must be doubled: thus CN *Gerhardt* = [C^2N *Hand-book*]; $C^3H^4O^2$ = [$C^4H^4O^4$]; C^8H^5NO = [$C^{16}H^5NO^2$]; C^2HCl^3O = [$C^4HCl^3O^2$]; C^2H^6S = [$C^4H^6S^2$], &c. 1 equivalent of water, according to Gerhardt, = H^2O = [2HO], and therefore not = 9 but = 18; similarly, 1 eq. carbonic oxide = CO = [2CO] and therefore not = 14 but = 28; 1 eq. carbonic acid = CO^2 = [$2CO^2$], therefore not = 22 but = 44; 1 eq. oil of vitriol = SH^2O^4 = [2(HO,SO^3)] therefore not = 49 but = 98; 1 eq. monohydrated nitric acid = NHO^3 = [HO, NO^5], therefore = 63 (as in the Hand-book), and 1 eq. hydrate of potash = KHO = [KO,HO] therefore = 56·2 (as in the Hand-book.)

That 18 water, 28 carbonic oxide, 44 carbonic acid, 80 sulphuric acid, &c., are the true equivalents, follows, according to Gerhardt, from this circumstance, that the quantity of water, carbonic oxide, or carbonic acid, given off in the decompositions of organic compounds is never merely 1 At. but always 2 At. (*Hand-book*) = 1 At. (*Gerhardt*), or a simple multiple thereof; moreover, that when organic compounds combine with water, sulphur, or sulphuric acid, the quantity of these substances thus taken up is never merely 1 At. (*Hand-book*) to 1 At. of the organic compound, but always 2 At. (*Hand-b.*) = 1 At. (*Gerhardt*), or a simple multiple thereof. Thus, oxalic acid, together with ammonia, forms oxamide, with separation of 2 At. (*Hand-b.*) water.

$$C^2HO^4 + NH^3 = C^2H^2NO^2 + 2HO.$$

Peppermint-camphor = $C^{20}H^{20}O^2$, when heated with anhydrous phosphoric acid, is converted into Menthene = $C^{20}H^{18}$ and 2HO, &c. On the other hand, common camphor = $C^{20}H^{16}O^2$ is converted, by taking up 2HO, into Campholic acid = $C^{20}H^{18}O^4$; similarly, Lactide = $C^6H^4O^4$, by addition of 2HO, is converted into Lactic acid = $C^6H^8O^6$, &c. [But the compound, $C^6H^6O^5$, which has likewise a separate existence, is converted into lactic acid by taking up merely 1 At. water (*Hand-b.*).] Further, Benzoic acid = $C^{14}H^6O^4$, when distilled with excess of lime, is converted into Benzol = $C^{12}H^6$, while $2CO^2$ remains in combination with the lime; and a large number of similar decompositions might be adduced, in which the quantity of carbonic acid separated amounts, not merely to 1 At. but to 2 At. (*Hand-b.*). Finally, all conjugated acids, consisting of sulphuric acid and an organic compound, contain for every 1 At. of the organic substance at least 2 At. and sometimes even 4 At. SO^3 (*Hand-b.*); but it is rarely that the combination takes place in equal numbers of atoms, as in sulphate of methyl = C^2H^3O, SO^3.

It is not to be denied that Gerhardt, in the determination of his so-called equivalents, has carried out the volume-theory in the most consecutive manner possible. This attempt, however, is open to the followin objections.

1. If the equivalents of sulphur and phosphorus are really twice as great as that of oxygen, the densities of the vapours of those elements ought also to be twice as great as that of oxygen gas. The latter is, in round numbers=1·1 (that of air=1·0); now, according to Dumas, the vapour-density of phosphorus is 4·4, and that of sulphur=6·65, whereas, according to Gerhardt, the vapour-density of both these elements should be only 2·2. Cahours, however, has found that certain organic acids, at temperatures just above their boiling points, have an anomalously high specific gravity, which, at higher temperatures, is reduced to the normal amount (*e. g.*, acetic acid at 125° has a vapour-density of 3·20, which at 338° is reduced to 2·08), and, moreover, that the vapour-density of sulphur, at a temperature 40° higher than that at which Dumas took it, is only 6·47; hence Gerhardt suggests (*N. J. Pharm.* 8, 288, II.) that, at a sufficiently high temperature, the specific gravity of sulphur-vapour would be reduced from 6·47 to 2·2, and that of phosphorus-vapour from 4·42 to 2·2, and thus the anomaly be removed. This, however, is highly improbable, first, because the difference is too great, and, secondly, because the behaviour of a few organic compounds, which present so many peculiarities, cannot give much information with regard to that of a simple substance.*

3. Gerhardt's atomic weights can scarcely be called *Equivalents;* at all events, this term, if applied to them, must be understood in a different sense from that in which Wollaston used it. Thus, according to the atomic weights assigned by Wollaston (and in this Hand-book) to chlorine and oxygen, these two substances are really equivalents; in CuO, 1 At. Cu may be replaced by 1 At. Cl, the result being a compound of the same order; and the aqueous solution of CuCl thus formed, behaves like a cupric salt. But, according to Gerhardt's atomic weights, 1 At. Cu requires, to bring it to the same order of combination, 1 At. Cl and only ½ At. O, or 2 At. Cu require 2 At. Cl and only 1 At. O; hence Cl and O are no longer *equivalent* one to the other.

3. Gerhardt's system introduces unnecessary complexity into the formulæ of chemical compounds: thus, Fe^2O^3 is converted into Fe^4O^3. Fe^3O^4 into Fe^6O^4; Cr^2O^3 into Cr^4O^3; CrO^3 into Cr^2O^3; CrO^2Cl into $Cr^2O^3Cl^2$; the last compound (which, according the atomic weights adopted in this work, may be regarded as chromic acid, in which 1 At. oxygen is replaced by 1 At. chlorine, or as a compound of 2 At. chromic acid with 1 At. terchloride of chromium), is evidently in strict analogy with chromic acid; moreover, according to our usual formulæ, CrO^3 and CrO^2Cl contain the same number of atoms; but, according to Gerhardt's formulæ (Cr^2O^3 and $Cr^2O^2Cl^2$), the number of atoms is 5 in the former and 6 in the latter, so that the analogy is destroyed. Similar irregularities likewise occur in organic compounds; thus, Gerhardt himself observes that alcohol and acetic acid, according to the ordinary formulæ, $C^4H^6O^2$ and $C^4H^4O^4$, contain equal numbers of atoms; whereas, according to his own formulæ, C^2H^6O and $C^2H^4O^2$, they contain different numbers, viz., alcohol 9 and acetic acid only 8 atoms; hence they cannot belong to the same type. And even if this be admitted, the resemblance between the two compounds is still too great to allow of the supposition that they contain different numbers of atoms.

4. The fact, that in most decompositions of organic compounds, in

* According to the more recent experiments of Bineau, the vapour-density of sulphur at a temperature about 1000° above its boiling point, is only one-third of that which it has a little above the boiling point. (Graham's Chemistry, 2nd Ed. I. 397.) [W.]

which water or carbonic acid is set free, the quantity of these compounds thus eliminated is not 1, 3, 5, or 7 At. (*Hand-b.*) but always 2, 4, or 6 At., does not really prove that 2 At. of water or carbonic acid should be reduced to 1 At., or, in other words, that the atomic weights of these compounds should be doubled, but is, in fact, merely a necessary consequence of the law already developed, according to which the greater number of organic compounds contain even numbers of atoms of carbon, hydrogen, and oxygen. If now an organic compound, when decomposed, yields carbonic acid and a new organic compound, also containing an even number of atoms, it follows of necessity, that an even number of atoms of carbonic acid, &c., must likewise be produced. Lastly, as we are obliged to double the atomic weights of many compounds, in order to make their number of atoms of carbon, &c., even, so likewise is this duplication required, to give greater generality to the assertion that the decomposition of organic compounds is attended with the evolution of an even number of atoms of carbonic acid, &c.

d. Suggestions respecting the Relative Position of the Elementary Atoms in a Compound Organic Atom, assuming the truth of the Nucleus-theory; by Gm.

The crude chemical formula of sulphate of potash is KSO^4, the rational formula is KO,SO^3, if the compound be regarded as sulphate of potash; K,SO^4 if it be regarded as sulphanide of potassium; and KS,O^4, if it be regarded as oxidized sulphide of potassium. Now whichever of these three rational formulæ be adopted, the mode of writing the formula gives no satisfactory idea of the manner in which the atoms are actually united. The three substances in the formula are arranged together in a straight line, *e. g.*, KO, SOOO; but in nature they are doubtless united into a body of three dimensions; for their mutual affinity induces the greatest possible approximation of the heterogeneous atoms. Nearly all chemists adopt the atomic theory; they determine the relative weights of the atoms, and their relative distances one from the other, or the relative space occupied by each atom of the combined substances, including the surrounding calorific envelope; hypotheses are also made respecting the form of the atoms, &c. Why then should we not likewise throw out suggestions with regard to their relative positions?

It may be assumed that the heterogeneous atoms in a compound will approach as near to each other as their mutual attraction or affinity requires, and the elasticity of the calorific envelope allows; and that they will take up that particular position with regard to each other, which allows of the greatest and most varied approximation of the heterogeneous atoms. Two atoms, such as HO, can only be disposed in a line. The same is true with regard to 2 At. of one substance and 1 At. of another, as MnO^2; here Mn lies in the middle, and 1 At. O to the right and left of it. One atom of a substance and 3 atoms of another, such as SO^3, probably form a plane triangle, with the sulphur-atom in the middle. With 1 At. and 4 At., as in NO^4, a tetrahedron may perhaps be formed, having the N in the middle and the 4O at the four summits of the figure. With 1 At. to 5 At., as in PO^5, P in the middle, 1O above, 1O below, and 3O disposed horizontally round P.

When these and similar compounds of the first order unite together,

e.g., to form salts, we may imagine that, in many cases, the relative position of the atoms no longer remains the same, but is so far altered that the tendency of the heterogeneous atoms to approximate as closely as possible is satisfied to the utmost. Thus, in the combination of KO with SO^3, a compound atom is probably formed, in which S is placed upon K, or *vice versâ*, and the 3 At. O horizontally around the points of contact. Similarly with KO,SO^3, excepting that in this case, the 4 At. O are placed in a square round the point of union of KS, so that a double four-sided pyramid is formed.* The tendency of the heterogeneous atoms to approximate as closely as possible, causes them to assume the most simple arrangement that their number will admit. That the crystals of sulphate of potash assume in spite of this arrangement of the double four-sided pyramid, a form belonging to the right prismatic, instead of the square prismatic system, arises perhaps from sulphur having a much larger atomic number than potassium (I., 55, 56), and consequently a much smaller specific volume or so-called atomic volume (I., 58), in consequence of which the vertices of the two pyramids are dissimilar.

This supposition respecting the aggregation of the atoms in sulphate of potash, may perhaps terminate the controversy as to whether that compound is KO,SO^3, or K,SO^4, or KS,O^4. According to the above hypothesis it is neither of the three, but rather KO^4S. The atoms, indeed, are united in such a manner that we cannot say which of the oxygen-atoms belongs to the K, and still less can we assert that the 4O belong to the S and not also to the K. At first view, it might appear that the third formula, KS,O^4, is admissible; but in sulphide of potassium, the K and S are probably more closely united than in sulphate of potash, in which the four surrounding oxygen-atoms interpose themselves to a certain extent between the K and the S. For the rest, until the above hypothesis shall have been put to the test of experience—which may best be done by comparing the crystalline forms of salts with the assumed form and arrangement of their atoms—preference must be given to the first of the three preceding formulæ, viz., KO,SO^3, inasmuch as it has always been adopted hitherto, and in the rest, the objections outweigh the advantages.—Oil of vitriol would, according to the same hypothesis, be similarly constituted, the K being merely replaced by H, &c.

This theory may perhaps lead to an explanation of the three isomeric states of phosphoric acid. The greater the number of atoms of any base (including water) which approach the acid—the metal of that base having a tendency to approach the phosphorus—the more are the oxygen-atoms surrounding the phosphorus thrust aside, and compelled to take up new positions with respect to the phosphorus and the metal. If now the phosphoric acid combined with 3 atoms of base, be deprived, first of one, and then of another atom of this base, the oxygen gradually returns to its former situation, from which it had been driven by the action of the base, and the monobasic acid thus produced can only be restored to the condition of a bibasic or terbasic acid, by the action of 2 or 3 atoms of a base assisted by heat or continued for a long time. $NaO,PO^5=NaPO^4$ is perhaps constituted similarly to KO,SO^3, excepting that 1 At. O is placed above the phosphorus-atom (this being supposed to be above the sodium) and another At. O, below the sodium-atom.—In $2NaO,PO^5$, we

* Readers who wish to make these considerations as clear as possible to themselves, are recommended to use balls of wax variously coloured, as representations of the atoms of the different elements.

have perhaps P in the middle; 1Na above and 1Na below the P; 1O above the upper Na, and 1O beneath the lower Na; and 5O arranged horizontally round the phosphorus.—In $3NaO,PO^5=Na^3PO^8$, we have 1O above and below the phosphorus-atom; 3 At. Na arranged horizontally in a triangle round the phosphorus-atom; and between these 3Na, likewise in horizontal planes, 3O above and 3O below.—Whether the arrangement of the atoms, here suggested be correct or not, the adherents of the atomic theory must at least admit that the atoms are not disposed in a line, like the letters in a formula, but that, by virtue of their affinity, they approach as closely as possible, thereby forming more or less regular, and generally solid figures; moreover, that it is of the utmost importance to make out this arrangement, as far as possible, with some degree of probability, since greater light may thereby be thrown on crystalline form, isomerism, and other relations, and since it is only by this means that we can hope to obtain correct views of the constitution of organic compounds, and decide the numerous existing controversies respecting the constitution of rational formulæ.

If now we apply to organic compounds the principles above illustrated, by examples taken from inorganic chemistry, and assume with Laurent, that these compounds may be divided into organic nuclei and compounds of these nuclei with substances externally attached to them, we shall find that, in the nuclei, the carbon-atoms must be united with the other atoms composing the nucleus, in such a manner as to allow the heterogeneous atoms to approach one another in as many ways as possible, whereby also a determinate figure must be produced, as Laurent has shown by the illustration given on page 14.

The nucleus, *Ethylene* (olefiant gas)$=C^4H^4$, may serve as an example. It has probably the form of a cube, four angles of which consist of C-atoms, and the four others diametrically opposed to them of H-atoms. In the secondary nuclei, from 1 to 4 At. hydrogen are replaced by other elements. To the ethylene-series belong, among many other compounds, aldehyde, alcohol, and acetic acid, the crude formulæ of which are: $C^4H^4O^2$, $C^4H^6O^2$, and $C^4H^4O^4$. These three compounds may, with some degree of probability, be supposed to contain the secondary nucleus C^4H^3O, one angle of the cube consisting of O. This cube-summit formed of an atom of oxygen may be called an *O-pole;* and the summit diagonally opposed to it and formed of carbon, a *C-pole.* According to this supposition, the rational formula of alcohol would be C^4H^3O,H^3O, consisting, in fact, of the secondary nucleus, C^4H^3O, with 3H and 1O externally attached. The 3H, in consequence of their peculiarly strong affinity for the O, are disposed on those three faces of the cube, one angle of which is formed by the O-pole, while the external O-atom places itself upon the carbon-pole, viz., the C-atom diametrically opposed to the O-atom of the nucleus, because it is most forcibly drawn into this position by the united action of the C- and H-atoms.

The rational formula of aldehyde, determined in a similar manner, is C^4H^3O,HO; the H-atom is attached to the O-atom of the nucleus, and the O-atom to the C-pole. The HO external to the nucleus is not by any means to be regarded as water, for the H and O are on the opposite poles of the cube. Hence the position of the atoms would be more correctly expressed by O,C^4H^3O,H in the case of aldehyde, and O,C^4H^3O,H^3 in that of alcohol; and these formulæ will perhaps be preferred, when we shall have succeeded in separating the nucleus-atom from the external atoms with greater certainty.

Acetic acid, $C^4H^4O^4$, would in the same manner be regarded as C^4H^3O,HO^3, or more precisely, as O^3,C^4H^3O,H,—3O being disposed on those three faces of the cube which consist only of C- and H-atoms, and 1H on the O-atom of the nucleus. The resulting figure is the same as for alcohol.

Ether = C^4H^5O is perhaps C^4H^3O,HH, one of the external H-atoms being placed upon the O-pole, the other on the C-pole.

These formulæ afford the most satisfactory explanations of many transformations in the ethylene-series, as the following examples will show:

Alcohol, by the action of 2O, is converted into aldehyde and 2HO; and this aldehyde, by the further addition of 2O, is converted into acetic acid. The first 2 At. O, together with 2H out of the three external H-atoms, form 2HO; the third of these external H-atoms is transferred from the cube-face to the O-atom of the nucleus, and in this manner aldehyde is formed. If 2O more are added, they dispose themselves on two of the cube-faces, consisting only of C and H, while the O-atom attached to the C-pole is transferred to the third cube-face, and thus acetic acid is formed.

2. When acetic acid, $C^4H^4O^4$, is neutralized with potash, the liquid evaporated, and the residue well dried, a compound is left, which may be denoted either, according to Laurent's system, as C^4H^3K,O^4, or, according to the binary theory, as $KO,C^4H^3O^3$ (*i. e.*, as a compound of potash with hypothetically anhydrous acetic acid). This compound, according to my view, is $C^4H^3O^4,KO^3$, or O^3,C^4H^3O,K; that is to say, the external atom H is replaced by K, with formation of water; whereas, according to Laurent's more recent system, all the H-atoms are situated in the nucleus, and the K enters the nucleus, taking the place of the H, yielding (C^4H^3K,O^4).— If the compound C^4H^3K,O^4 be again evaporated to dryness with a fresh portion of potash-solution, no more water is formed or eliminated; the potash, amounting to more than 1 At. for 1 At. of acetic acid, remains perfectly unaltered. How is it now that the potassium can replace 1 At. H, and not the other three? This peculiarity is explained when we adopt for acetic acid the formula C^4H^3O,HO^3. Only the one H-atom which is external to the nucleus, can be replaced by potassium; the 3 atoms within the nucleus cannot. As with potash, so is it likewise with the other metallic oxides consisting of 1O and 1 Metal; and as with acetic acid, so is it with the rest of the more definite monobasic acids.

3. An opposite relation is apparent in the action of chlorine on acetic acid. For, under certain circumstances, 6 At. Cl and $C^4H^4O^4$ form 3 At. HCl, and chloracetic acid = $C^4HCl^3O^4$, three atoms of chlorine taking the place of the three hydrogen-atoms, which are converted into HCl; the chloracetic acid thus formed is not altered by contact with a larger quantity of chlorine. In this case, it is obvious that the H-atom which is replaceable by a metal, remains unaltered; for the chloracetic acid, when neutralized with potash and evaporated, yields $C^4Cl^3KO^4$, with separation of 1 At. HO. Hence chloracetic acid is C^4Cl^3O,HO^3, and chloracetate of potash is C^4Cl^3O,KO^3.

This difference of comportment between the one H-atom and the other three is explained by their different arrangement. The one external atom which can be replaced by a metal, touches only the O-atom of the nucleus; and when it combines with the oxygen of a metallic oxide and escapes in the form of water, the metal attaches itself to the O-atom of the nucleus.

Moreover, in consequence of the very close proximity which exists between the simple atoms of an organic compound, it is probable that the result is determined, not only by the affinity of the atoms lying immediately together, but also, though in a less degree, by that of the more distant atoms; and therefore, in the present case, not only by the affinity of the O-atom in the nucleus for the hydrogen on the one hand and the metal on the other, but also by that of the more distant atoms of C and H in the nucleus, and the three O-atoms external to it.

In all cases in which a metallic oxide forms with acetic acid, the compound $C^4H^3MO^4$, the action being attended with separation of water, we may imagine that the affinity of the H for the O of the metallic oxide *plus* the affinity which the compound C^4H^3O,O^3 (*i. e.*, the acetic acid *minus* the external atom of H,) exerts upon the metal through the medium of the oxygen-summit of the nucleus, *plus* the affinity of heat for the HO, tending to form vapour with it (in case of heat being necessary), is greater than the affinity of the metal for the oxygen *plus* the above-mentioned affinity of the C^4H^3O,O^3 for the H. Similarly, with other acids. This separation of water does not take place with every acid and every metallic oxide; in many cases not even at the strongest heat. Metallic oxides appear to be unable to act on the three H-atoms of the nucleus, because these atoms are immediately surrounded by carbon-atoms, which probably have much less affinity for metals than for hydrogen.

On the other hand, chlorine does not act upon the H-atom external to the nucleus, because the neighbouring O-atom has a very strong affinity for the H, and very little for the Cl; or more exactly: the affinity of C^4H^3O,O^3, as it acts at the O-pole of the nucleus, for H, is greater than the affinity of the same to one atom of chlorine + the affinity of another atom of chlorine for the H. But the chemical relations of the chlorides of carbon, show that the affinity of chlorine for carbon is somewhat considerable; hence it is possible that the affinity of 3 At. Cl for 3H of the nucleus *plus* the affinity of 3 other At. Cl for the C-atoms of the nucleus may overcome the affinity of 3H for the latter.

4. When chlorine converts alcohol C^4H^3O,H^3O into chloral, $C^4HCl^3O^2 = C^4Cl^3O,HO$, two atoms of chlorine first abstract 2 At. H external to the nucleus and leave aldehyde $= C^4H^3O,HO$ (the third external atom of hydrogen, being at the same time transferred from the cube-surface to the O-atom of the nucleus, is thereby withdrawn from the influence of the chlorine); afterwards 3 more atoms of chlorine abstract 3H from the nucleus, and 3 other atoms of chlorine take their place. The product thus obtained is chloral $= C^4HCl^3O^2 = C^4Cl^3O,HO$, in which, therefore, as in chloracetic acid, the secondary nucleus C^4H^3O is converted into C^4Cl^3O. Liebig (*Ann. Pharm.* 19, 274) gives to aldehyde and chloral the formulæ C^4H^3O,HO and C^4Cl^3O,HO; but he regards the HO as water actually formed; whereas in my view, the H of the HO is supposed to be situated at the O-pole, and the O at the C-pole of the nucleus.

5. Alcohol heated with excess of oil of vitriol is resolved into 2HO, and olefiant gas $= C^4H^4$. In this case, the predisposing affinity of the sulphuric acid for the water causes the O-atom in the nucleus and the O-atom external to it to unite with 2H to form water, whilst the third external atom of H takes the place of the single O-atom of the nucleus, and thus reproduces the primary nucleus:

$$C^4H^3O,H^3O = C^4H^4 + 2HO.$$

With a smaller quantity of oil of vitriol, the products are ether and only 1 At. water = $(C^4H^5O,H^2)+HO$. In this case, only 1O and 1H external to the nucleus combine to form water, and 2H remain without it.

6. When chlorine acts upon this ether = C^4H^5O,HH, there are produced: first, the compound C^4H^5O,HCl (the H going to the O-pole, the Cl to the C-pole); secondly, C^4H^5O,Cl^2 (that the external atom of hydrogen at the O-pole is in this case abstracted by Cl, while the same does not take place in acetic acid, may, perhaps, be explained by the consideration, that in the latter, there are 3 O-atoms to weaken the attraction of the C and H in the nucleus for the Cl which seeks to place itself at the O-pole); and lastly, C^4Cl^5O,Cl^2, the 3H in the nucleus being likewise replaced by chlorine.

7. Strong hydrochloric acid heated with alcohol forms hydrochloric ether = C^4H^5Cl, with separation of 2HO; or,

$$C^4H^5O,H^2O+HCl=C^4H^5Cl,HH+2HO.$$

Here the external O-atom unites with an external H-atom, and the O-atom of the nucleus with the H of the hydrochloric acid to form 2HO, while the Cl takes the place of the O-atom in the nucleus.

8. Finally, to consider one of the most complicated cases, the formation of a compound ether: Alcohol and acetic acid form 2 At. water and 1 At. acetic ether, the decomposition, according to the empirical formulæ, taking place as follows:

$$C^4H^6O^2+C^4H^4O^4=C^8H^8O^4+2HO.$$

Here we must suppose that the carbon-pole of the alcohol first approaches the oxygen-pole of the acetic-acid, so that the former may give up the external O-atom there situated to the external H-atom on the O-pole of the acetic acid; in the next place, the alcohol and acetic acid—a cube-face of the one being turned towards a cube-face of the other—must turn round in such a manner, that the C-pole of the alcohol and the O-pole of the acetic acid may move away from one another, and the O-pole of the alcohol and the C-pole of the acetic acid approach one another. In this movement, one of the three external H-atoms surrounding the O-pole of the alcohol, comes in contact with one of the external O-atoms surrounding the C-pole of the acetic acid; these atoms unite in the form of a second atom of water, and are eliminated; and the cube-face of the alcohol thereby exposed attaches itself to the simultaneously exposed cube-face of the acetic acid; and in this manner 1 At. acetic ether is produced. Hence this compound, being formed by the juxtaposition of two cubes, has the form of a square prism. On two of the opposite lateral edges of this prism, there are situated in succession, supposing the acetic acid to be at the top, CHCH; on the third: OCHC; on the fourth: HCOC. On this last edge, however, there are likewise two external O-atoms belonging to the acetic acid, at the top, and two external H-atoms, belonging to the alcohol, at the bottom, so that this edge exhibits the following arrangement: $H\overset{O}{O}CO\overset{H}{H}C$ (the atoms here placed on the left are supposed to be actually at top). The formula is therefore:

$$C^4H^5O,H^2O+C^4H^5O,HO^2=2HO+(C^4H^5O,H^2+C^4H^5O,O^2).$$

Acetic ether contains therefore an alcohol-residue = C^4H^5O,H^2 combined

with an acetic acid residue = C^4H^3O,O^3. In short, in the formation of acetic ether, the alcohol and the acetic acid both lose 1HO, but in such a manner that 1O of the alcohol combines with 1H of the acetic acid, and 1H of the alcohol with 1O of the acetic acid to form 2 Aq. This alcohol-residue, although it has the same composition as ether, is nevertheless not identical with that compound. In the alcohol-residue of the acetic ether, the two external H-atoms are situated on two cube-faces at the C-pole; in ether, one of the atoms of hydrogen is placed at the O-pole, the other at the C-pole.—Acetic ether, when treated with aqueous solution of potash, is reconverted into alcohol and acetate of potash. Here we may suppose, that the K from the KO attaches itself externally to the acetic acid residue, converting it into C^4H^3O,KO^2, and the O to the C-pole of the alcohol residue, which is thereby converted into C^4H^3O,H^2O; moreover, that these two products, which have no separate existence, decompose 1HO, the O of which is employed in completing the formation of acetate of potash, C^4H^3O,KO^3, and the H in completing the formation of the alcohol, C^4H^3O,H^3O.

9. Oxalic acid dried at 100° = C^2HO^4; as thus considered, it is monobasic, and forms with 1 At. PbO, C^2PbO^4 and 1 Aq. It may, however, be regarded as bibasic, a supposition probable for several reasons; and then its atomic weight must be doubled. The crude formula will then be $C^4H^2O^8$. According to the latter view, it likewise belongs to the ethylene-series, excepting that its secondary nucleus consists only of C and O. It may then be regarded as C^4O^4,H^2O^4. The 4C are united with the 4O into a cube; the 2 At. H being probably situated on two of the opposite faces of this cube, and 4O on the other four sides. If 1NaO comes in contact with this compound atom, the H of one cube-face is replaced by 1Na, with formation of water, and the acid salt is produced, which, after drying at a strong heat, has, according to the binary theory, the composition $NaO,C^2O^3 + HO,C^2O^3$ or NaO,HO,C^4O^6, or, according to Laurent, C^4HNaO^2,O^6, and, according to the view here developed, must be written in the form $C^4O^4,HNaO^4$. When 2NaO comes in contact with the oxalic acid, both the atoms of hydrogen situated on the opposite faces of the cube are replaced by Na, and the neutral salt is formed, which, according to the binary theory, is NaO,C^2O^3 or $2NaO,C^4O^6$; according to Laurent, $C^4Na^2O^2,O^6$; according to the view now under consideration, C^4O^4,Na^2O^4.—Oxalic acid with 2 At. alcohol forms oxalic ether and 4 At. HO:

$$2(C^4H^3O,H^3O) + C^4O^4,H^2O^4 = 4HO + [2(C^4H^3O,H^2) + C^4O^4,O^2].$$

The process is similar to that which takes place in the formation of acetic ether: 1 At. alcohol transfers the O-atom situated at its C-pole, to the H-atom on one of the cube-faces of the oxalic acid; then, as the nucleus turns round, 1 H-atom of the three which are situated round the O-pole is transferred to an O-atom on a second cube-face of the oxalic acid; while the cube-face of that substance from which the H has been abstracted attaches itself to a cube-face of the alcohol; and similarly with a second atom of alcohol. In this manner, a square prism is formed, composed of three cubes, the oxalic acid being in the middle; two external H-atoms are attached to each of the two alcohol-residues, and two external O-atoms to the oxalic acid residue (= C^4O^4,O^2).

Laurent's *Palene*- or *Methylene*-series includes among other compounds:

Marsh-gas=C^2H^4; methylic ether=C^2H^3O; wood-spirit=$C^2H^4O^2$; formic acid $C^2H^2O^4$. In this case, we may suppose that methylene has the shape of a square table, the four corners of which are formed of a C-atom and an H-atom alternately. In marsh-gas, two more atoms of H are attached to the nucleus, making C^2H^2,H^2; of these 2H, one is attached to the upper, the other to the lower surface of the square table; and if the figure be so placed that one of the C-atoms shall be above and the other below, the 4H will be arranged horizontally round the point of contact of the 2C, so that an octohedron will be formed. Methylic ether, C^2HO,H^2, has for its secondary nucleus a square table formed of 2 C-atoms, 1 H-atom, and 1 O-atom placed opposite to the H-atom, and having also 1 At. H attached to the middle of its upper and under surface; the same construction, therefore, as for marsh-gas. Wood-spirit = C^2HO,H^2O, has the same form as methylic ether, excepting that one additional O-atom is attached to the H-atom of the nucleus, and one H-atom to the O-atom of the nucleus. Formic acid is C^2HO,HO^2, and therefore contains the same secondary nucleus, C^2HO; an O-atom is placed above and below at the middle of the square table; also 1 O-atom with the H-atom of the nucleus, and 1 H-atom with the O-atom of the nucleus. Hence it appears that wood-spirit and formic acid have exactly the same structure, corresponding externally to an acute square-based octohedron, excepting that in wood-spirit the base of the figure is formed of 2C and 2H, and in formic acid of 2C and 2O; just as (p. 33) the structure of an atom of alcohol is similar to that of an atom of acetic acid. When formic acid = C^2HO,HO^2 is converted by PbO into HO and formiate of lead = C^2HO,PbO^2, an atom of Pb is introduced into the place of the H-atom attached to the O-atom of the nucleus.

These examples taken from the ethylene- and the methylene- series may suffice, for the present, to give a general idea of the view which I entertain of the constitution of organic compounds. With a few exceptions, it is essentially the same as Laurent's nucleus-theory, and may be regarded as a further extension and confirmation of that theory by an investigation of the relative positions of the elementary atoms. Even if the data of this investigation are defective or erroneous, I am yet convinced, that all theories on the constitution of organic compounds, and all controversies as to this or that mode of writing rational formulæ, if not supported by a plausible arrangement of the compound atom, will aid us but little in the acquisition of correct ideas. Look, for instance, at the controversy respecting the constitution of ether and alcohol between Dumas and Boullay on the one side, and Berzelius and Liebig, on the other. According to the former, ether is a compound of etherine with water=C^4H^4,Aq., and alcohol=C^4H^4,2Aq.; according to the latter, the hypothetical radical, ethyl=C^4H^5, forms with O, the oxide of ethyl= ether; and this, with the addition of 1 At. water, forms the hydrated oxide of ethyl=alcohol=C^4H^5O+Aq. Now, on comparing these views with the explanation given on page 32, it appears probable that neither of them is right. At all events, neither ether nor alcohol can be supposed to contain water ready formed; they are not hydrates; if so, they would surely give up this water to burnt lime or baryta, which, however, is not the case. Neither is ether converted into alcohol by solution in water. On the other hand, ethyl is a fictitious compound (see p. 12), supposed to combine like a metal with oxygen and with chlorine, forming compounds analogous to the metallic oxides and chlorides. Thus

hydrochloric ether=C^4H^5Cl (=C^4H^3Cl,H^2. *Gm.*) is regarded as chloride of ethyl; but it does not precipitate silver-solutions, &c.

II. Formation of Organic Compounds.

We have to distinguish between the formation of these compounds from inorganic materials, and their formation from a previously existing organic substance.

1. *Formation of Organic Compounds from Inorganic Materials.*

This process takes place chiefly in living plants. Vegetables elaborate the greater part of the organic compounds of which they consist from the inorganic materials presented to them; chiefly from water, carbonic acid and ammonia. In the green parts of plants, during the presence of light, decomposition of carbonic acid, and, to a certain extent also, of water, is constantly going on; and while the whole or a part of the oxygen is given off in the form of gas, the remaining portion enters into an organic compound.

Thus, we may suppose that, for the formation of oxalic acid (=$C^4H^2O^8$), 4 At. CO^2 and 2HO are required; $4CO^2+2HO=C^4H^2O^{10}$; and when 2O are evolved, there remains $C^4H^2O^8$=oxalic acid. For the formation of common sugar (supposing that compound = $C^{24}H^{22}O^{22}$), $24CO^2$ and 22HO are required; if the $24CO^2$ give all their oxygen, viz. 48O, there remain 24C, which, in a manner not yet explained, combine with the 22H and 22O of the 22HO to form sugar.—In other cases, oxygen appears to be given off from water as well as from carbonic acid. Thus, $20CO^2$ and 16HO, when they give off all their oxygen, yield 20C and 16H, which unite and form oil of turpentine.—To give an example of the manner in which an azotized body may be conceived to be formed in a plant, we will suppose, with Mulder, that protein=$C^{40}H^{31}N^5O^{12}$. In that case, $40CO^2$, 16HO, and 5 ammonia, will be required to form it, and from these compounds 84O must be separated:

$$40CO^2+16HO+5NH^3-84O=C^{40}H^{31}N^5O^{12}.$$

Numerous transformations of one chemical compound into another likewise take place in living plants as well as in animals. [For further details on this subject, *vid. Chemical Physiology of Plants and Animals.*]

Art is but rarely able to produce organic compounds from inorganic materials, but is competent to transform a given organic compound into a great variety of others.

The following are examples of the artificial production of organic compounds from inorganic materials.

1. Although nitric acid is generally produced by the decay of azotized organic bodies, and ammonia by their decay or destructive distillation, both these substances may nevertheless be formed by processes purely inorganic; a mixture of 2 vol. nitrogen and 5 vol. oxygen gas, subjected

for some weeks to the action of the electric spark, while standing over water, yields aqueous nitric acid (II., 387). When tin is acted upon by aqueous nitric acid, nitrate of ammonia is formed, together with other products (II., 418). If this salt be then converted into sal-ammoniac, the latter intimately mixed with black-lead and lime or oxide of lead, and the mixture heated in a retort,—or, if a mixture of ammoniacal gas and carbonic oxide be passed through a red-hot tube, &c., *hydrocyanate of ammonia* passes over, and the hydrocyanic acid, which is the first organic compound thus formed, may afterwards be converted into several others. Thus, the hydrocyanate of ammonia, distilled with dilute sulphuric acid, will yield *aqueous hydrocyanic acid*=HC^2N; on saturating this compound with mercuric oxide, crystallizing by evaporation, and heating the resulting crystals of cyanide mercury=Hg,C^2N, by themselves, we obtain gaseous *cyanogen*=C^2N. Finally, on passing this gas into aqueous ammonia, by which it is abundantly absorbed, we obtain, among other products, *oxalic acid*=$C^4H^2O^8$, and *urea*=$C^2H^4N^2O^2$. The aqueous hydrocyanic acid, heated with sulphuric acid or with potash, is resolved into ammonia and *formic acid*=$C^2H^2O^4$. Besides these compounds, there may be formed from the hydrocyanic acid, paracyanogen, cyanuric acid, sulphocyanogen, mellon, and various other organic compounds. [For further details, *vid. Cyanogen.*]

2. The carbon in cast iron yields organic compounds when the cast iron is treated in various ways.

a. When cast iron is dissolved in dilute sulphuric or hydrochloric acid, a fetid gas is evolved, the odour of which is due to the vapour of a volatile oil mixed with the gas (V., 216, 217). Part of the hydrogen, as it escapes from the water in the *nascent state*, appears to combine with the carbon separated from the cast iron, to form this oil. The vapour of the same oil appears also to be mixed with the offensive, empyreumatic, fatty-smelling hydrogen gas which Kastner (*Kastn. Arch.* 2, 239) obtained by passing vapour of water over cast-iron nails (previously softened by ignition between ferric oxide) heated to redness in a gun-barrel.

b. When cast iron is thus dissolved in sulphuric or hydrochloric acid, a residue is left, which, besides graphite, contains a brown, mould-like substance, soluble in potash (V., 216, 217). A similar mould-like substance is left on dissolving cast iron in nitric acid or aqua-regia (V., 216). Part of this substance passes into solution with the ferric oxide; is thrown down, together with the oxide, on the addition of ammonia; and may be dissolved out from the precipitate by boiling water or aqueous potash. (Berzelius, *Afhandlingar*, 3, 128; also *Scher. Ann.* 7, 234; further, *Lehrb.* Aufl. 5, B. I., 739.) In the formation of this mould-like substance, the carbon separated in the nascent state by the solution of the iron, appears to unite with H and O derived from the water.

c. When the alloy of 1 pt. platinum and 100 steel (VI., 336) is dissolved in dilute sulphuric acid, and the insoluble residue, containing platinum, iron, carbon and hydrogen, is boiled, there remains a blackish substance no longer soluble in the acid; this, after being washed and dried, detonates slightly and with a faint light at about 200°, and, as the heat gradually rises, decomposes without further detonation. The same substance dissolved in aqua-regia yields a very large quantity of platinum and a small quantity of iron. (Faraday and Stodart, *Ann. Chim. Phys.* 21, 72.) In the production of this phenomenon, there is doubtless an organic compound concerned, probably containing hyponitric acid. (Gm.)

3. The carbon contained in bisulphide of carbon is also capable of yielding organic compounds.

a. When the anomalous compound $CSCl^2O^2$, discovered by Berzelius and Marcet, and produced by the action of chlorine and water on bisulphide of carbon (II., 337), is digested at a gentle heat with baryta-water, a solution of BaCl is obtained, together with a baryta-salt containing $BaO,C^2Cl^3S^2O^5=C^2BaCl^3,S^2O^6$:

$$2(CSCl^2O^2) + 2BaO = BaCl + C^2BaCl^3,2SO^3.$$

The acid of this salt has, in the uncombined state, the formula, $C^2HCl^3,2SO^3$. Now this acid may, by the action of re-agents which abstract chlorine and substitute hydrogen in its place, *e.g.*, by zinc, and by the electric current at the negative pole—be first converted into $C^2H^2Cl^2,2SO^3$, then into $C^2H^3Cl,2SO^3$, and finally into $C^2H^4,2SO^3$. All these acids may be regarded as conjugate acids containing for every 2 At. sulphuric acid, 1 At. marsh-gas$=C^2H^4$, in which the hydrogen is partly replaced by chlorine.

If, now, we regard this substance C^2H^4, thus combined with the sulphuric acid, as organic, we must conclude that an organic product has been formed from inorganic materials, and the question then arises, where does this formation begin? Is sulphide of carbon an organic compound$=C^2S^4$? Or is Berzelius and Marcet's compound to be regarded as $C^2Cl^4,2SO^3$, *i.e.*, as a compound of sulphurous acid with an organic chloride of carbon? Or does the organic formation begin with the four acids above mentioned? The first and second of these suppositions are the most probable. The peculiar camphor-like nature of the $CSCl^2O^2$ inclines us to suppose that this compound is organic. But there are also many reasons for regarding even sulphide of carbon as an organic compound. Its specific gravity is much less than the mean between the specific gravities of its constituents (I., 72), and there is no example of such expansion in the case of an inorganic compound. It likewise exhibits remarkably great volatility in comparison with its constituent elements. Lastly, it yields a number of other organic compounds (*vid. inf. b* and *c*). But, if sulphide of carbon be regarded as an organic compound, we lose the analogy which this substance and carbonic acid exhibit in their saline compounds. Carbonate of potash$=KO,CO^2$; but sulphocarbonate of potassium will no longer be KS,CS^2, but $2KS,C^2S^4$, &c. Hydrosulphocarbonic acid CHS^3 (II., 206) would then be the acid of this potassium-salt, and $=C^2H^2S^6$. On such a supposition, the analogy can only be restored, by doubling the atomic weight of carbonic acid, and thereby converting it into a bibasic organic acid: Monocarbonate of potash$=2KO,C^2O^4$; bicarbonate of potash$=KO,HO,C^2O^4$. But carbonic acid does not exhibit any real similarity with the organic acids, which, in the free state, contain a number of atoms of hydrogen equal to the number of atoms of metal which they take up to form a salt; there is no acid having the composition $C^2H^2O^6$ or $2HO,C^2O^4$, and analogous to hydrosulphocarbonic acid. Lastly, if we regard carbonic oxide as C^2O^2, phosgene as $C^2Cl^2O^2$, and suppose that cast-iron, a substance formed at a white heat, contains (together with free iron) an organic compound of C and Fe, which, when the iron is dissolved in acids, exchanges its iron for H or H and O,—we shall be led to consider all carbon-compounds as organic, and may then perhaps agree with Gerhardt in making the atomic weight of iron$=12$.—How far we may safely go in this direction must be decided by further investigations.

b. When vapour of sulphide of carbon is passed, together with chlorine, through a red-hot porcelain tube, chloride of sulphur and chloride of carbon=CCl^3 [C^2Cl^4, *Gm.*] are produced; the latter, when purified and passed by itself through a red-hot porcelain tube, yields chlorine gas and a mixture of CCl and C^2Cl^3 [C^4Cl^4 and C^4Cl^6; for compounds containing but few atoms of carbon may be converted by a red heat into compounds containing many carbon-atoms: *Gm.*] This CCl [C^4Cl^4] being covered with a stratum of water, and exposed to sunshine in a bottle filled with chlorine, is for the most part converted into C^2Cl^3 [C^4Cl^6], but part of it is transformed into chloracetic acid [$C^4HCl^3O^4$]. (Kolbe, *Ann. Pharm.* 54, 147, and 181). By the action of potassium dissolved in mercury and also by water, this chloracetic acid may be converted into ordinary acetic acid=$C^4H^4O^4$. (Melsens, *N. Ann. Chim. Phys.* 10, 233.) Thus acetic acid is formed from sulphide of carbon. This acid may then be converted into acetone, $C^6H^6O^2$, cacodyl, and various other organic compounds.

c. Aqueous ammonia, with sulphide of carbon, forms hydrosulphocyanate as well as hydrosulphocarbonate of ammonia.

4. When potassium is prepared by distilling carbonate of potash with charcoal, the carbonic oxide gas as it escapes, carries with it a yellowish grey vapour which condenses in the form of a yellowish grey substance in the delivery tube (III., 7). This substance dissolves in water, forming a reddish yellow solution, from which *rhodizinate* (Gm.; Heller), *croconate* (Gm.), and *oxalate* of potash (Liebig, *Schw.* 47, 114; also *Mag. Pharm.* 15, 141; Gm. *Pogg.* 7, 525; also *Mag. Pharm.* 15, 140) may be obtained. Moreover, the dark brown mother-liquor of these salts contains a large quantity of a potash-salt, the acid of which is *humic*, or some similar acid, together with small quanities of *acetate* of potash, *formiate* of potash, and *cyanide* of potassium (Gm.). *Tartrate* of potash, the presence of which is mentioned by Liebig, I was not able to find. Since, according to Liebig, rhodizinate and croconate of potash may likewise be obtained by passing carbonic oxide gas over heated potassium, it follows that these acids are not formed directly from the charcoal or from the rock-oil used in the preparation of the potassium, but by the action of potassium-vapour on carbonic oxide gas at a lower temperature.

5. Wood-charcoal boiled for some time with dilute nitric acid, dissolves and forms a brown liquid, which, on evaporation, leaves a brown extract soluble in water; it precipitates a solution of glue, and is therefore called *artificial tannin*. (Hatchett.) The same reaction is obtained with charcoal prepared from inorganic substances, viz., by decomposing carbonate of soda with phosphorus at a red heat. (Gm.)

Döbereiner (*Oken's Isis*, 1817, s. 576; further, *Gilb.* 58, 210) observed that when vapour of water is passed in considerable quantity over charcoal heated to redness in a gun-barrel, the gas-delivery tube being surrounded with cold water, a gelatinous, volatile substance, which smells like fat and is soluble in water, collects in the tube and ultimately stops it up.

This experiment did not succeed in the hands of Bérand and Trommsdorff. (*N. Tr.* 2, 2, 203.)

A mixture of 1 vol. carbonic acid gas and 1 vol. carbonic oxide, or of 2 vol. carbonic acid and 1 vol. hydrogen, placed over aqueous solution of potash, either in the light or in the shade, does not yield oxalic acid; neither is sugar formed by strongly compressing a mixture of equal measures of carbonic acid gas and marsh-gas. (Döbereiner, *Gilb.* 59, 323; 75, 338.)

On the whole it appears that only the lower order of organic compounds, those, namely, which contain but few atoms of carbon, can be formed artificially from inorganic materials; in the mould-like substances, however, which are obtained from cast-iron and in the preparation of potassium, a larger number of carbon-atoms is supposed to be present.

2. *Formation of one Organic Compound from Another.*

Many transformations of this kind take place in living plants and animals, but art is likewise capable of converting a given organic compound into a great variety of others. Many of these artificially formed organic compounds likewise occur in nature.

The following compounds, for example, may be formed by artificial processes:—*Formic acid;* from tartaric acid, oxide of manganese, and sulphuric acid.—*Oxalic acid,* from sugar and nitric acid.—*Acetic acid,* in various ways.—*Butyric acid,* from sugar, by a peculiar kind of fermentation.—*Valerianic acid,* from potato-oil, by the action of fused hydrate of potash.—*Succinic acid,* by treating fatty substances with nitric acid.—The volatile oil in the flowers of *Spiræa ulmaria,* from salicin and chromic acid.—The volatile oil of *Gaultheria procumbens* (salicylate of methyl), from salicylic acid and wood-spirit.—*Grape-sugar,* from starch or woody fibre, by sulphuric acid.—*Margaric acid,* from stearic acid by distillation.—*Urea,* from cyanic acid and ammonia, or from uric acid by the action of peroxide of lead.—*Allantoin,* from uric acid by peroxide of lead.

The number of artificially formed organic compounds which do not occur in nature, is however immeasurably greater. Among these may be mentioned: Methylic alcohol, methylic ether, and many other members of the methylene-series; nearly all the members of the ethylene-series; the members of the phenylene-series, &c.;—so that, taking into account the numerous compounds in which H is artificially replaced by Cl, Br, I, Ad, or X, we may say that the organic compounds which can only be obtained artificially, far exceed in number those which occur in nature. Lately, indeed, chemists have even succeeded in forming artificial alkaloids, *e. g.*, melamine, ammeline, aniline, chinoline, lophine, furfurine, thiosinnamine, sinnamine, sinapoline, napthalidam.

But in most cases of the artificial formation of one organic compound from another, the number of carbon-atoms either remains the same or diminishes, the latter phenomenon being equivalent to the depression of the compound to a lower rank in the scale. In some few cases, on the contrary, we can by artificial processes, convert compounds containing a smaller number of carbon-atoms, into others containing a greater number. If now we consider that art is capable of producing certain organic compounds from inorganic materials, and in some cases, also, of increasing the number of carbon-atoms in a given organic compound, it appears not impossible that we shall some day be able to form artificially, many if not all the organic compounds which occur in nature.

In many cases, however, the increase in the number of carbon-atoms by artificial process is only apparent.

In the actual *increase in the number of carbon-atoms,* the product richer in carbon must be a primary organic compound; the symmetrical figure in which the constituent atoms are arranged, must not appear like an aggregate of several figures, but must have a common centre.

This actual increase in the number of carbon-atoms is most readily brought about by strong heat.

When benzoate of lime, $C^{14}H^5CaO^4$, is heated to redness in a retort, or when vapour of alcohol, ether, or creosote is passed through a red-hot tube, naphthaline, $C^{20}H^8$, is formed. Hence, $C^4H^6O^2$, C^4H^5O, or $C^{12}H^6O^2$, yields $C^{20}H^8$; the carbon of 5 At. alcohol, for example, must therefore be employed in forming 1 At. naphthaline. At a red heat, carbon separates from the organic vapours in the form of soot; and at the moment of separation from one part of the organic compound, it appears to pass over to another part in order to form therewith a compound richer in carbon. Even if naphthaline be regarded as C^5H^2 it will still contain 1 At. of carbon more than alcohol; but this formula is inadmissible, being inconsistent with the boiling point, vapour-density, compounds, and substitution-products of naphthaline: for instance, it would require that $C^{20}H^7Cl$, should be expressed fractionally: $C^5H^{\frac{7}{2}}Cl^{\frac{1}{2}}$.

The destructive distillation of wood, &c., yields paraffine$=C^{48}H^{50}$, whereas wood is generally supposed to contain only 24 At. C.

C^2Cl^4 passed through a red-hot tube, yields in addition to free chlorine, two kinds of chloride of carbon, which must be regarded, not as C^3Cl^3 and C^3Cl^5, but as C^4Cl^4 and C^4Cl^6; for both may, by a process, in which there is no reason to suppose that any increase of carbon-atoms takes place, be converted into chloracetic and afterwards into acetic acid, in which the existence of 4C must be admitted (p. 41).

If oxalic acid be regarded, not as monobasic$=C^2HO^4$, but as bibasic$=C^4H^2O^8$, the transformation of formiate of potash into oxalate by heating it with a mixture of lime and hydrate of potash, must be regarded as a change of the same nature:

$$2(C^2KHO^4) \quad C^4K^2O + H^2.$$

In the same light also, we must consider the formation of oxalic acid by the action of cyanogen, C^2N, on aqueous ammonia.

In the dry distillation of acetates, an empyreumatic oil is obtained $=C^{10}H^6O$, or more probably$=C^{20}H^{16}O^2$, whereas an atom of acetic acid contains only 4 At. C.

Fusel-oil, $C^{10}H^{12}O^2$, may be converted, by distillation with phosphoric acid at a gradually increasing heat, first into $C^{10}H^{10}$, then into $C^{20}H^{20}$, and lastly into $C^{40}H^{40}$.

Another transformation of the same kind is the conversion of lactic acid, $C^6H^6O^6$, into butyric acid, $C^8H^8O^4$, by a peculiar fermentation.

$$2(C^6H^6O^6) = 4H + 4CO^2 + C^8H^8O^4.$$

Also the brown resin into which aldehyde is converted by the action of potash, and the resinous and coaly products which oil of vitriol forms with many organic compounds, doubtless contain in one atom a larger number of carbon-atoms than the compounds from which they are formed.

In the *apparent increase of the number of carbon-atoms*, organic compounds or parts of them are made to unite, to the number of two or more atoms, so as to form a complex product, in which the number of carbon-atoms is consequently increased. But the resulting complex compounds, Laurent's *Syndesmides*, may again be resolved into the original compounds containing the smaller number of carbon-atoms.

Urea, when subjected to a moderately strong heat, is converted into ammonia and cyanuric acid, which latter compound is supposed to contain three times as many carbon-atoms as urea:

$$3(C^2H^4N^2O^2) = 3NH^3 + C^6H^3N^3O^6.$$

Hydrosulphocyanate of ammonia heated nearly to redness in a close vessel, yields Mellon = C^6N^4.

Crude bitter almond oil, $C^{14}H^6O^2$, is converted by certain modes of treatment, into compounds, which, according to Laurent, contain 2, 3, 4, 6, and even 9 times as many carbon-atoms. A few examples may serve to elucidate this matter. Bitter almond oil is converted, by the action of hydrosulphate of ammonia, into Sulphobenzene:

$$C^{14}H^6O^2 + 2HS = C^{14}H^6S^2 + 2HO;$$

And this compound, when subjected to dry distillation, yields, among other products, crystalline laminæ of Stilbene = $C^{28}H^{12}$. This compound might be regarded as the hitherto unknown nucleus of bitter almond oil and benzoic acid, that is to say, as Benzene = $C^{14}H^6$. But, according to this formula, its vapour would be monatomic (2 volumes); whereas, according to the formula $C^{28}H^{12}$, it is diatomic (4 volumes). The latter view is also confirmed by the substitution-products of stilbene, *e. g.*, $C^{28}H^{11}Cl$ and $C^{28}H^{11}X$. In the oxidation of stilbene by chromic acid, however, it is brought back to the degrees of oxidation of benzene, viz., into bitter almond oil, $C^{14}H^6O^2$, and benzoic acid, $C^{14}H^6O^4$. Moreover, bitter almond oil freed from hydrocyanic acid is converted by aqueous ammonia into rectangular octohedrons of Hydrobenzamide, $C^{42}H^{18}N^2$, in which 3 At. benzene $C^{14}H^6$, are united with 2N. This compound, by contact with cold aqueous hydrochloric acid, is converted into bitter almond oil and sal-ammoniac:

$$C^{42}H^{18}N^2 + 6HO + 2HCl = 3(C^{14}H^6O^2) + 2(NH^4Cl).$$

In a similar manner, Isatin = $C^{16}H^5NO^4$ may be transformed into compounds in which 2, 3, or 6 atoms of it are united.

3 At.-Mellitic acid = $3(C^4HO^4)$ with 1 At. ammonia form Euchronic acid = $C^{12}H^2NO^8$, with separation of 4HO; but the latter compound, when heated to 200° in contact with water, is again resolved into 3 At. mellitic acid and 1 At. ammonia.

Oil of turpentine, exposed to the air, is converted into a resin containing twice as many carbon-atoms:

$$2(C^{20}H^{15}) + 6O = C^{40}H^{30}O^4 + 2HO;$$

to suppose that this resin has the composition $C^{20}H^{15}O^2$, would be inconsistent with its slight volatility, and with the proportion in which it combines with bases. In this case, perhaps, a real augmentation of the number of carbon-atoms takes place.

The class of *Syndesmides* likewise includes those compounds which are regarded as *Acetones in the general sense* (*Ketones?*). When acids containing 4O are made to combine with potash, and the dry salt is heated in a retort, carbonate of potash remains and the acetone passes over. Thus 2 At. acetate of potash are resolved into 2 At. carbonate of potash and 1 At. acetone, properly so called.

$$2(C^4H^3KO^4) = 2(KO,CO^2) + C^6H^6O^2.$$

Here, then, we have a 6-carbon compound produced from a 4-carbon

compound. The former may, however, be regarded as a compound of the second order, consisting of the residues of 2 At. acetic acid, viz., $C^4H^4O^3 + C^1H^2$. For by the action of oxidating agents, an acid is produced containing, not 6 but 4 C-atoms, viz., acetic acid. Similar observations might be applied to other products of the same class (vid. *Decomposition of organic compounds by fixed alkalis*).

In the same category must be included the various compound ethers, formed, with separation of water, by treating an alcohol with an organic acid. In these compounds, the number of C-atoms is equal to the sum of the C-atoms in the alcohol and the acid; but they are not primary organic compounds; and when treated with aqueous alkalis, they are again resolved into alcohol and acid.

Gerhardt and Laurent, in order to get rid of all uneven numbers of atoms, suppose that when only 1 At. H comes in contact with 1 At. of a compound, 2 At. of the compound unite with 2H. Thus, by addition of 1H, alloxan $C^8H^4N^2O^{10}$, is converted into alloxantin, $C^8H^5N^2O^{10}$; chinone, $C^{12}H^4O^4$, into green hydrochinone, $C^{12}H^5O^4$; indigo-blue, $C^{16}H^5NO^2$, into indigo-white, $C^{16}H^6NO^2$; they therefore write the crude formulæ of the hydrogenated compounds as follows: $C^{16}H^{10}N^4O^{20}$; $C^{24}H^{10}O^8$; $C^{32}H^{12}N^2O^4$. Further proofs are, however, required to establish the necessity of this duplication.

III. Properties of Organic Compounds.

1. State of Aggregation.—But few organic compounds, those, namely, which contain but a small number of C- or H-atoms, and little or no O or Cl; such as C^2H^4, C^4H^4, C^6H^6, C^3H^3O, C^2H^3Cl, are *gaseous* at 0°.

The following are *mobile liquids:* Wood-spirit, alcohol, ether, most compound ethers of the methylene and ethylene series, acetone, lignone, &c.

The following are *viscid liquids:* Some compound ethers, most volatile oils, some fats, many alkaloids not containing oxygen, a few acids, such as lactic acid, certain saccharine matters, such as glycerine and gum-sugar.

Example of *glutinous* substances are found in the soft resins and caoutchouc.

By far the greater number of organic compounds are *solid* at 0°, and among these the majority are *crystallizable.* Several of them may be obtained both in the crystalline and in the amorphous state, and in that case, they exhibit two different melting points, the lower of which belongs to the amorphous state.

When sylvic acid, lithofellic acid, common sugar, or amygdalin is cooled after fusion at a gentle heat, it solidifies in a vitreous mass. In this state it has by no means lost its power of crystallization, but exhibits a lower boiling point, which, however, cannot be determined with precision, because the amorphous mass, before solidifying, passes into the viscid state. The melting point of crystallized sylvic acid is 140°; that of the amorphous acid, between 50° and 100°; of lithofellic acid, the two melting points are 205° and 105°—110°; of sugar, 160° and 90°—100°;

and of amygdaline, 200° and 125°—130°. (Wöhler, *Ann. Pharm.* 41, 155; also *Pogg.* 53, 259.)

When part of the hydrogen in an organic compound is replaced by Cl or Br, the compound sometimes retains the same crystalline form. This is the case with oxamethane = $C^8H^7NO^6$, and chloroxamethane = $C^8Cl^5H^2NO^6$. (Prevostaye). Berzelius (*Jahresb.* 21, 402) lays too little stress on this relation.—Similarly the compounds $C^{20}H^8,Cl^4$, and $C^{20}H^7Cl,Cl^4$ (the latter being crystallized from ether) exhibit the same form, with the exception of slight differences in the angles. These small angular differences are sometimes produced even by treating a hydrocarbon, first with bromine and then with chlorine, or contrariwise; so that ultimately the same compound is produced, having part of its H replaced by Br and Cl, only that, in the one case, the Br-atoms fill up the places of those H-atoms which have first been removed, and the Cl-atoms, the places of those which have last been removed; while in the other case, the substitution is effected in the contrary order.

Thus, when naphthaline, $C^{20}H^8$, is first treated with bromine, so that $C^{20}H^6Br^2$ is produced, and afterwards with chlorine, the final product is $C^{20}H^4Br^2Cl^2$; but if the process be begun with chlorine, the ultimate product is $C^{20}H^4Cl^2Br^2$. Both these compounds crystallize in oblique rhombic prisms; but in the former, the angles of the faces are 101° 30′, 102° 50′, and 101° 15′; in the latter, 102° 10′, 103°, and 101° 20′. Such compounds, possessing similar crystalline forms and the same stoichiometric composition, but with the individual atoms of the elements in different places, are called *Isomeromorphous*. (Laurent, *Compt. rend.* 14, 350; 20, 1590.) For the establishment of this isomeromorphism, however, further proofs are desirable; for the small angular differences which have been observed may result from inequality of the crystalline faces, &c. Until the position of the H-atoms in naphthaline is determined, it is impossible to decide whether the two hydrogen-atoms first withdrawn have a different value to the other two.

2. The Specific Gravity of organic compounds in the liquid or solid state, lies between 0·627 (the most volatile of the empyreumatic oils from oil-gas), 1·75 (tartaric acid), 1·92 (hydriodic ether), and 2·237 (iodide of methyl). Compounds containing nothing but carbon and hydrogen are the lightest; those which are most rich in oxygen, chlorine, bromine, and iodine, are the heaviest.

Calculation of the Specific Gravity of Liquid Organic Compounds.

According to the explanations given in Vol. I., pp. 58 and 74, the so-called *Atomic Volume* or *Specific Volume* signifies the quotient obtained by dividing the atomic weight of a substance, either simple or compound, by its specific gravity; this quotient expressing, in fact, the relative volume occupied by 1 At. of the substance, together with its thermic envelope. If the atomic weight of the substance = G; its specific gravity = D, and its specific volume = V, we have

$$G = D \cdot V;$$

that is to say, the atomic weight of any substance varies directly as the space occupied by an atom of the substance, together with its thermic envelope, and directly also as the density of the substance, and consequently

as the specific gravity of the specific volume. The above equation gives further:

$$\frac{G}{D} = V; \text{ and } \frac{G}{V} = D;$$

that is to say, the atomic weight divided by the specific gravity, gives the specific volume, and the atomic weight divided by the specific volume, gives the specific gravity. Further, we may assume, according to this volume theory, that (with certain limitations), the specific volume of a compound is equal to the sum of the specific volumes of its constituents. Upon this theorem, first enunciated by Schröder, depends the application of the volume-theory to the specific gravity of organic compounds, an application which is, however, subject to important exceptions in particular cases. As the result of these endeavours to calculate the specific gravity of a substance from its composition is still very unsatisfactory, it may suffice, for the present, to give a short exposition of the different ways in which Kopp, Schröder, and Löwig, have endeavoured to solve this problem. In this exposition I shall make use of the atomic weights adopted in the present work; consequently all numbers having reference to the assumption: O = 100, H = 6·25, &c. will be altered.

Kopp's Theory.—We must, in the first place, determine the specific volumes of carbon, hydrogen, and oxygen. The great variations in the specific gravity, and consequently in the specific volume of organic liquids, produced by change of temperatures, render it necessary to fix upon some standard temperature; and for this purpose, the boiling point under a given pressure is perhaps the best adapted. This will be seen from the following calculation of the specific volumes of water, ether, and alcohol: Alcohol, $C^4H^6O^2$, may be regarded as a compound of ether, C^4H^5O, with water, HO. According to Gay-Lussac's determinations, the specific gravities of water, ether, and alcohol, at their boiling points, are 0·961, 0·695, and 0·739: if now we divide these specific gravities by the atomic weights of the three substances, which are 9, 37, and 46, we obtain their specific volumes, viz., 9·37, 53·24, and 62·25, and by adding together the specific volumes of water and ether, we obtain that of alcohol very nearly: 9·37 + 53·24 = 62·61. Consequently, 1 At. water, at its boiling point, and 1 At. ether at its boiling point, take up together the same space as 1 At. alcohol at its boiling point. If now we take the specific gravities of these three liquids at 10°, or any other temperature, the same accordance is by no means evident; because at 10°, or any other given temperature, they are removed from their boiling points by a very different number of degrees. But the agreement still exists when the specific gravities of the three liquids are taken at equal distances from their boiling points, *e. g.*, that of water at 100° − 20° = 80°; that of ether at 35·4° − 20° = 15·4°; and that of alcohol at 78·4° − 20 = 58·4°. These temperatures, equi-distant from the boiling points, are called *corresponding temperatures.* (*Pogg.* 56, 371.) As there is considerable difficulty in determining the specific gravities of liquids at their boiling points, it is best to make the determination at equal distances below those points, *i. e.*, at corresponding temperatures. This method is not, perhaps, quite accurate, because different liquids, in cooling a given number of degrees below their boiling points, may contract in such a manner that the mutual relations of their specific volumes no longer remain the same.

It is found that, in organic compounds, the specific volume of hydrogen

is equal to that of oxygen [at least in the same series: *Gm.*]; for two compounds containing equal numbers of carbon-atoms, but different numbers of hydrogen and oxygen-atoms,—the differences, however, being such that the sum of the H- and O-atoms is the same in both,—have equal specific volumes; *e. g.*, acetic acid $= C^4H^4O^4$, and alcohol $= C^4H^6O^2$; similarly, aldehyde $= C^4H^4O^2$, and ether $= C^4H^5O$. Hence 1 At. hydrogen, with its thermic envelope, takes up as great a volume as 1 At. O, with its thermic envelope, although the oxygen-atom is eight times as heavy.

The specific gravity of water at its boiling point is 0·9616; and if we divide 9 (the atomic weight of water) by this number, we obtain 9·36 as the specific volume of HO. Assuming then that H and O have equal specific volumes, it follows that the specific volume of water must be produced from 1 sp. vol. H = 4·68, and 1 sp. vol. O = 4·68.

The atomic weight of alcohol, $C^4H^6O^2$, is $24+6+16=46$; its specific gravity at the boiling point = 0·739; and $46 \div 0{\cdot}739 = 62{\cdot}2$. Hence the specific volume of alcohol is 62·2. Now, in alcohol, 4 sp. vol. C are united with 6 sp. vol. H and 2 sp. vol. O; and if from the sp. vol. of alcohol = 62·2, we substract the sum of 6 sp. vol. hydrogen and 2 sp. vol. oxygen, viz. $8 \times 4{\cdot}68 = 37{\cdot}44$, there remains 24·76 ($62{\cdot}2 - 37{\cdot}44 = 24{\cdot}76$) for 4 sp. vol. carbon. Hence the specific volume of carbon = 6·2.—A similar calculation with ether gives for the specific volume of carbon, the number 6·28; and the mean of these numbers, viz., 6·24, is taken as the real specific volume of that element. (Atomic weight of ether, $C^4H^5O = 24+5+8=37$; sp. gr. at boiling point = 0·695; $37 \div 0{\cdot}695 = 53{\cdot}2$; $53{\cdot}2 - 6 \,.\, 4{\cdot}68 = 25{\cdot}12$; $25{\cdot}12 \div 4 = 6{\cdot}28$.)

It appears, then, that at the boiling points of liquids, the specific volume of C = 6·24, and of H and O = 4·68. These numbers are in the ratio of 4 : 3; and, consequently, the sp. vol. of C may be denoted by $4 \,.\, 1{\cdot}56$, and that of H and O = $3 \,.\, 1{\cdot}56$; and when, by the cooling of the liquids, the specific volumes of the carbon, hydrogen, and oxygen contained in them are diminished, the ratio of the C-volume to the H- and O-volume remains the same, viz., 4 : 3; we may suppose, therefore, that the 4 and 3 remain unaltered, and the diminution falls wholly on the common factor, 1·56.

Ether boils at 35·7, and from its specific gravity at that temperature, its specific volume is found to be 53·2; at −19·3°, that is to say, 55° below its boiling point, its sp. gr. is such that the sp. vol. is reduced to 49°. Hence by cooling 55° below its boiling point, the specific volume of ether is reduced from 53·2 to 49; and the specific volumes of its three constituent elements are simultaneously reduced in the same proportion, viz., C from 6·24 to 5·76; H and O, from 4·68 to 4·32; Or: the common factor, 1·56, is diminished, as the liquid cools down 55° below its boiling point, from 1·56 to 1·44; for $4 \,.\, 1{\cdot}44 = 5{\cdot}76$, and $1{\cdot}44 \,.\, 3 = 4{\cdot}32$. Since then, by a reduction of 55° below the boiling point, the common factor is diminished by 0·12 ($1{\cdot}56 - 1{\cdot}44 = 0{\cdot}12$), it would appear that for a reduction of temperature equal to 1°, the diminution of the factor must be 0·00218; but since in calculations relating to other liquids, the diminution of the specific volume comes out somewhat less, it is admitted, as a mean result, that the common factor 1·56, which corresponds to the boiling point of the liquid, diminishes by 0·0016 for each degree below the boiling point.

Thus, the sp. vol. of carbon, at a certain number of degrees ($= d$) below the boiling point $= (4 \,.\, 1{\cdot}56 - d \,.\, 0{\cdot}0016)$, and that of hydrogen and oxygen $= (3 \,.\, 1{\cdot}56 - d \,.\, 0{\cdot}0016)$. For an organic compound containing

a At. C, *b* At. H, and *c* At. O, the formula for calculating the specific volume at a given temperature is therefore:

$$(4a+3b+3c) \;.\; (1{\cdot}56 - d \;.\; 0{\cdot}0016).$$

(*Ann. Pharm.* 55, 197). The specific volumes of C, H, and O, at different degrees below the boiling point, are given in the following table, in which the number of degrees below the boiling point is denoted by *d*, and the specific volumes of oxygen and hydrogen, being equal, are put together in the same column:

d.	C	H and O	*d.*	C	H and O	*d.*	C	H and O
0°	6·24	4·68	110°	5·54	4·15	220°	4·83	3·62
10	6·18	4·63	120	5·47	4·10	230	4·77	3·58
20	6·11	4·58	130	5·41	4·06	240	4·70	3·53
30	6·05	4·55	140	5·34	4·01	250	4·64	3·48
40	5·98	4·49	150	5·28	3·96	260	4·58	3·43
50	5·92	4·44	160	5·22	3·91	270	4·49	3·38
60	5·86	4·39	170	5·15	3·86	280	4·45	3·34
70	5·79	4·34	180	5·09	3·82	290	4·38	3·29
80	5·73	4·30	190	5·02	3·77	300	4·32	3·24
90	5·66	4·25	200	4·96	3·72	310	4·26	3·19
100	5·60	4·20	210	4·90	3·67			

From this table, we may calculate the specific gravities of organic liquids consisting of C and H, or of C, H, and O at any required temperature, when their composition and boiling points are known. As an example, take acetic acid = $C^4H^4O^4$, which boils at 118°. What is its specific gravity at 16°, that is, at 102° below its boiling point? At that temperature, 1 sp. vol. C = 5·585; and 4 . 5·585 = 22·34; 1 sp. vol. H and O = 4·19; and 8 . 4·19 = 33·52; hence 22·34 + 33·52 = 85·56 = the specific volume of acetic acid. If now we divide the atomic weight of acetic acid = 60, by this number, we obtain 1·074 for the specific gravity of acetic acid at 16°. Experiment gives 1·063, differing somewhat considerably from the calculated result; many of the examples calculated by Kopp exhibit similar and even greater differences.

The specific volumes of the other elements which occur in organic liquids are more difficult to determine. Kopp estimates that of chlorine by calculation from chlorobenzide, $C^{12}H^5Cl$, as equal to 21·84 at the boiling point, or 14 (1·56 − *d* . 0·0016) at other temperatures. The specific volumes of nitrogen and sulphur are still more uncertain.—According to this mode of calculation, any two isomeric organic liquids should have equal specific gravities at equal distances from their boiling points,—a result empirically obtained by Aubergier with respect to the oils which are isomeric with oil of turpentine. (Kopp, *Ann. Pharm.* 50, 71.)

Before publishing the preceding general theory, Kopp had laid down the following particular laws (*Ann. Pharm.* 41, 79 and 169), which the general theory now serves to explain: (1.) The specific volume of an acid is less by 24 than that of the compound ether which the acid forms with wood-spirit, and less by 43 than that of the ether which it forms with alcohol. The general theory gives for acetic acid the following numbers: Acetic acid = $C^4H^4O^4$; acetate of methyl = $C^6H^6O^4$; acetate of ethyl = $C^8H^8O^4$. The specific volume of acetic acid = 4 . 6·24 + 8 . 4·68 = 62·40; that of acetate of methyl contains 2 sp. vol. C, and 2 sp. vol. H in addition, = 12·48 + 9·36 = 21·84; the sp. vol. of acetate of ethyl contains

4 sp. vol. C and 4 sp. vol. H more than acetic acid, therefore $4 \cdot 6{\cdot}24 + 4 \cdot 4{\cdot}68 = 43{\cdot}68$. Hence, according to the general theory, acetic acid when converted into acetate of methyl, increases in specific volume by 21·84, and when converted into aceic ether, by 43·68; now the law (1) empirically found gives the approximate numbers 24 and 43.

(2.) The specific volume of every ethyl-compound is greater by 18·7 than that of the corresponding methyl-compound.—Now methyl is C^2H^3, and ethyl, C^4H^5; the latter, therefore, contains C^2H^2 more than the former; this makes $2 \cdot 6{\cdot}24 + 2 \cdot 4{\cdot}68 = 21{\cdot}84$, which is not very far from 18·7; &c. (Kopp; *comp.* also Rieckher, *Ann. Pharm.* 46, 222); also Kopp (*Chem. Soc. Qu. J.* 3, 104).

Schröder's Theory.—The specific volumes of C, H, and O may be supposed to be equal, and may be calculated from that of alcohol. This substance $= C^4H^6O^2$, contains 2 double atoms of C, 3 double atoms of H, and 1 double atom of O, making together 6 double atoms. [The double atoms of H here spoken of are twice as great as those assumed by Berzelius.] If now the atomic weight of alcohol, 46, be divided by its specific gravity at the boiling point = 0·7395, we obtain 62·2 for the specific volume of alcohol at its boiling point; and dividing this by 6, we have 10·379 for the specific volume of a double atom of C, H, or O. From this, we may easily calculate the specific volume, and thence the specific gravity of any organic compound consisting of C, H, and O, taking account, however, as in Kopp's theory, of the distance from the boiling point; for, at 10° below the boiling point, the specific volume of alcohol is only 10·262; at 20° below the same point, 10·136; at 30°, 10·022; at 40°, 9·905; at 50°, 9·794; at 60°, 9·693; at 70°, 9·601, &c.; hence, to obtain the specific volume of 1 double atom of C, H, and O, at a given distance from the boiling point of any liquid, these numbers must be divided by 6.*

Example: Wood-spirit, $C^2H^4O^2$, boils at 60°; it contains 4 specific volumes of double atoms; its atomic weight $= 12 + 4 + 16 = 32$. The specific volume of a double atom at 40° below the boiling point of a liquid is 9·908; this, taken 4 times, gives 39·62 for the specific volume of wood-spirit at 40° below its boiling point, that is to say, at 20°; and dividing the atomic weight = 32, by the specific volume, 39·62, we obtain 0·808 for the specific gravity of wood-spirit at 20°; observation gives 0·798. Most of the other examples calculated by Schröder and collected in a table, give results more exact than this; but in some the differences are even greater. In these calculations, the atomic weights of organic compounds must be taken in such a manner, that one atom of them may yield 4 volumes of vapour or a diatomic gas (p. 53); hence ether must be not C^4H^5O, but $C^8H^{10}O^2$. (*Pogg.* 62, 341.)—Kopp (*Pogg.* 63, 311) remarks that these calculations give very good results, although, according to his own theory, the specific volume of C is to that of H and O as 4 : 3, and not as 1 : 1; this anomaly, however, is explained by the consideration that the specific volume which Schröder assigns to a simple atom, viz., $\frac{10{\cdot}262}{2} = 5{\cdot}19$, is very nearly a mean between Kopp's sp. vol. of a C-atom = 6·84, and that of an H- or O-atom = 4·68, and consequently in calculating the specific volumes of organic compounds, the proportion of the C-atoms to the H- and O-atoms, remains nearly the same.

* There is an error here: the numbers 10·262, 10·136, &c. evidently denote, not the specific volumes of *alcohol*, but the specific volumes of the *double atoms* of C, H and O, at the distances 10°, 20°, &c. below the boiling point. [W.]

Löwig's Theory (Chemie der org. Verbindungen, 91).—The specific volumes of the different elements stand in close relation to their atomic weights; if the atomic weights of H, C, O, N, and Cl=1, 6, 8, 14, and 36, the atomic volumes will be 1, 3, 4, 7, and 9 (corresponding to a twofold and fourfold condensation of the thermic envelope surrounding the atoms). Putting O=100, Löwig estimates the specific volumes of H=44, C=132, N=308, O=176, &c. But in organic compounds, the volume of the hydrogen may be condensed to $\frac{3}{4}$, $\frac{1}{2}$, and $\frac{1}{4}$, whereby it is reduced from 44 to 33, 22, or 11. In certain organic compounds, the volumes of the other elements above-mentioned, may, besides these three condensations, suffer a condensation to $\frac{2}{3}$ and $\frac{1}{3}$.—Example: Benzin, $C^{12}H^6$, has a specific gravity of 0·85; its atomic weight (O=100) is 12 . 75 (atomic weight of C)+6 . 12·5 (atomic weight of H)=950; and 950÷0·85=1147 (sp. vol. calculated from the sp. gr., O=100). If now we add together 12 sp. vol. of carbon condensed to two-thirds, viz., 12 . 88, and 6 sp. vol. of hydrogen condensed to one-half, viz., 6 . 22, we obtain a sum=1188, which is the specific volume of benzin. This calculated specific volume, however, is greater than that which is obtained from the observed specific gravity, and, therefore, the specific gravity obtained by dividing the atomic weight by this specific volume, is not the same as the sp. gr. determined by experiment, but a smaller number, viz., 0·821.

Very important, if confirmed by further examples, would be Löwig's observation, that the specific volume of a compound is not altered by addition of oxgen; *e. g.*, Aldehyde, $C^4H^4O^2$; atomic weight=44; sp. gr. at 18°=0·79; and Acetic acid, $C^4H^4O^4$; atomic weight=60; sp. gr. at 16°=1·063; hence the sp. vol. of aldehyde=44÷0·79=55·7, and that of acetic acid=60÷1·063=56·4. The agreement, however, is not so great as it appears to be; for the specific gravity of acetic acid is taken 102° below its boiling point, and that of aldehyde only 3° below; at 99° below the boiling point, the sp. gr. of the latter would be much greater, and, therefore, its specific volume much smaller, and accordingly differing more widely from that of acetic acid. On comparing Oil of Turpentine ($C^{20}H^{16}$, atomic weight 152; sp. gr. 0·87; boiling point 157°), Camphor ($C^{20}H^{16}O^2$, atomic weight 152; sp. gr. 0·986; boiling point 204°), and Camphoric acid ($C^{20}H^{16}O^8$; atomic weight 200; specific gravity 1·194; boiling point 270°), we find the specific volume of Oil of Turpentine=156; of Camphor=154, and of Camphoric acid=167. Similarly the specific volumes of Valeral, $C^{10}H^{10}O^2$ and Valerianic acid, $C^{10}H^{10}O^4$ are nearly=105 and 108. These calculations, therefore, seem to agree very well with the above-mentioned law of Löwig relating to oxygen.

With regard, however, to the general character of Löwig's mode of calculating specific volumes and specific gravities, it is easy to see that, since the specific gravities of most organic compounds lie between 0·800 and 1·400, and consequently the range of variation does not exceed 0·600, and since, moreover, these compounds contain the same elements in different proportions, while the specific gravities of the elements themselves probably vary but little, it is not very surprising that the specific gravity of an organic compound should admit of calculation within 0·010 (and sometimes even this degree of approximation is not attained), especially when we take the specific volumes of the elements somewhat arbitrarily, and assume to ourselves the liberty of imagining, when necessary, that they are condensed in the compound to $\frac{3}{4}$, $\frac{2}{3}$, $\frac{1}{2}$, $\frac{1}{3}$, and $\frac{1}{4}$.

On the whole, indeed, when we consider that Kopp, Schröder, and more especially Löwig, proceed from assumptions differing so widely one

from the other, and, nevertheless, each one is of opinion that specific gravities may be rightly determined according to his method, we cannot but feel considerable mistrust of all these attempts, and of the so-called theory of atomic volumes altogether. If either one be right, both the others must be wrong. In the earlier attempts to solve this problem, the discrepancies between observed and calculated specific gravities, were attributed to the unequal expansion of different compounds by heat; but now that this source of error has been removed in the case of liquids, by taking the specific gravities, &c., at corresponding temperatures below the boiling point, it is but reasonable to expect, that observation and calculation should agree exactly; such, however, is not the case, either in the theory of Kopp, or in that of Schröder or Löwig.

Specific Gravity of Organic Compounds in the Gaseous State, or Vapour-density of Organic Compounds.

An organic compound, considered in the gaseous state, always occupies a smaller volume than its elements would occupy in the free state, supposing them to exist in the gaseous form at the same temperature, and under the same pressure; hence, in the formation of an organic compound, condensation always takes place, and moreover in a simple ratio.

In some rare instances, the entire volumes of the elements, supposed to be in the gaseous state, are united into one volume of the compound (also in the gaseous state). Thus 1 vol. of gaseous cyanogen, C^2N, contains 2 vol. hypothetical carbon-vapour and 1 vol. nitrogen gas. The gas of the compound is therefore monatomic, that is to say, the number of atoms of the compound contained in 1 vol. of the gas is equal to the number of hydrogen-atoms contained in 1 vol. hydrogen gas. The specific gravity of an organic gas thus constituted may therefore be found by adding together the specific gravities of the gaseous elements, the specific gravity of each of them, if it be monatomic, being taken as many times as there are atoms of the element in the compound, and half as many times if it be 2-atomic.

In most cases, however, the entire volumes of the gaseous elements are united into 2 volumes of the organic compound. The compound then forms a ½-*atomic* or *diatomic* gas, that is to say, a gas which, in a given volume, contains only half as many atoms of the compound as the same volume of hydrogen gas contains of hydrogen-atoms. These organic compounds are usually said to form 4 volumes of vapour (*vid. inf.*). In this case the specific gravity of the organic gas is obtained as above, by adding together the specific gravities of the gaseous elements, and dividing the sum by 2.

We must here call to mind the hypotheses laid down on page 53, Vol. I. of this Hand-book respecting the volumes of gases: the atoms of the elements in the gaseous state are surrounded with thermic envelopes of various sizes; those of the sulphur-atoms are the smallest; those of the oxygen-, phosphorus-, and arsenic-atoms, are 3 times as large, and those of hydrogen, nitrogen, chlorine, bromine, iodine, &c., 6 times as large: or, in other words, a space which contains 1 . x At. hydrogen, nitrogen, chlorine, &c., in the gaseous state, will contain 2 . x At. oxygen, &c., and 6 . x At. sulphur (all these substances being supposed to be in the gaseous state, and at equal temperatures and pressures). If then hydrogen gas, &c., be called monatomic, oxygen gas will be 2-atomic and

sulphur-vapour 6-atomic.* Carbon-vapour, which doubtless exists above a certain temperature, is hypothetically supposed to belong to the monatomic gases, and accordingly its sp. gr. is by calculation=0·4160, that of air being 1·000. Many other chemists, however, regard carbon-vapour as 2-atomic, and accordingly make its sp. gr.=0·8320.

The following are examples of the calculation of the specific gravities of diatomic organic gases.

	Marsh-gas.			*Oil of Turpentine.*			*Alcohol.*		
	At.	Vol.	Density.	At.	Vol.	Density.	At.	Vol.	Density.
C-vapour	2	2	0·8320	20	20	8·3200	4	4	1·6640
H-gas	4	4	0·2772	16	16	1·1088	6	6	0·4158
O-gas							2	1	1·1093
Org. Compound	1	2	1·1092	1	2	9·4288	1	2	3·1891
Vapour-density			0·5546			4·7144			1·5945

The 2 At. oxygen in the alcohol, enter as only 1 vol. of gas, inasmuch as oxygen is a 2-atomic gas. It appears then that in marsh-gas, for example, 2 At. C. are united with 4 At. H. to form 1 At. marsh-gas, which, in the gaseous state occupies 2 volumes; these two volumes weigh 1·1092; consequently, the weight of 1 volume, or the specific gravity of the gas is 1·1092÷2=0·5546 (the sp. gr. of air=1·0000). Hence 1 At. marsh-gas occupies twice as large a space as 1 At. hydrogen; or a space which would include 1 . x At. hydrogen, contains only $\frac{1}{2}$. x At. marsh-gas. If then hydrogen gas be called monatomic, marsh-gas must be diatomic.

Other chemists make the atomic weight of hydrogen only half as great, and the specific gravity of carbon-vapour, not=0·416 as in this Hand-book, but=0·832 (supposing it to be 2-atomic, like oxygen gas): on these hypotheses the preceding table will be altered as follows:

	Marsh-gas.			*Oil of Turpentine.*			*Alcohol.*		
	At.	Vol.	Density.	At.	Vol.	Density.	At.	Vol.	Density.
C-vapour	2	2	1·6640	20	20	16·6400	4	4	3·3280
H-gas	8	8	0·5544	32	32	2·2176	12	12	0·8316
O-gas							2	2	2·2186
	1	4	2·2184	1	4	18·8576	1	4	6·3782
			0·5546			4·7144			1·5945

According to this theory, the elements form, by their combination, *four* volumes of organic gas; hence the often occurring expression that most (or all) organic compounds form 4 volumes of vapour. In this system, therefore, an organic compound of 4 vol. gas or vapour is equivalent to that which in the present Hand-book is designated as an organic compound, whose gas or vapour is $\frac{1}{2}$-*atomic* or *diatomic*. The origin of the difference is, that in the first-mentioned mode of calculation, the volume of an atom of any organic compound, in the gaseous state, is compared with the volume of 1 At. hydrogen in the form of gas, and in the last-mentioned, with the volume of 1 At. oxygen in the gaseous state.

* According to Bineau's experiments, sulphur-vapour is 2-atomic like oxygen gas. (See note, p. 29.)

If we adopt the system of Dumas, and suppose the atomic weight of O, C, and H = 100 : 37·5 : 6·25 = 8 : 3 : ½, the sp. gr. of carbon-vapour will still be 0·416, and the numbers in the table which denote the volumes of carbon-vapour will be doubled, viz., 4 vol. carbon-vapour in marsh-gas, 40 in oil of turpentine, and 8 in alcohol.

A few organic compounds form monatomic instead of diatomic gases, viz., cyanogen, ether, carbonic ether, and one or two others.

Cyanogen.			*Ether.*			*Carbonic Ether.*		
	At.	Vol.	Density.	At.	Vol.	Density.	At.	Vol.	Density.
C	2	2	0·8320	4	4	1·6640	5	5	2·0800
N	1	1	0·9706	5	5	0·3465	5	5	0·3465
				1	½	0·5546	3	1½	1·6639
	1	1	1·8026	1	1	2·5651	1	1	4·0904

No division by 2 is here required; the sum of the specific gravities of the elementary gases is equal to the specific gravity of the organic compound in the gaseous state. Such exceptions from the rule may in most cases be removed by doubling the atomic weights; thus, ether may be written: $C^8H^{10}O^2$, and carbonic ether: $C^{10}H^{10}O^6 (= 2C^4H^5O + 2CO^2)$. In the case of cyanogen, however, there are considerable objections to this duplication.

In some very rare cases, almost confined to certain organic acids, the vapour of an organic compound, when its density is taken near the boiling point, is found to contain ⅔ as many atoms in a given volume as hydrogen gas. But the farther above the boiling point the determination is made, the more nearly does the density, in consequence of an increase in the rate of expansion, approach to that of a diatomic gas.

If the vapour of acetic acid $C^4H^4O^4$ be regarded as diatomic, calculation gives its specific gravity as follows:

	Vol.	Sp. gr.
C-vapour	4	1·6640
H-gas	4	0·2772
O-gas	2	2·2186
	2	4·1598
	1	2·0799

But Dumas (*Ann. Pharm.* 27, 138) found the sp. gr. of acetic acid vapour to be 2·74. Now ⅔ of 4·1598 = 2·7732; hence Dumas concluded that the mode of condensation in acetic acid is different from that which takes place in other organic compounds, the vapour being in fact condensed into 3 instead of 4 volumes. Similarly, Bineau found (*Compt. rend.* 19, 767; also *J. pr. Chem.* 33, 423) that the sp. gr. of acetic acid vapour at temperatures between 129° and 132°, varies from 2·78 to 2·86. It has, however, been found by Cahours (*Compt. rend.* 19, 771; also *J. pr. Chem.* 33, 427) that when the heat is raised considerably above the boiling point, 120°, the anomaly disappears. According to his experiments, the specific gravity of acetic acid vapour at 145° is equal to 2·75, but at 219°, it is 2·17; in another specimen of acetic acid, the sp. gr. at 231° was found to be 2·12. This last number corresponds almost exactly to the calculation above given. Finally, Cahours has shown (*Compt. rend.* 19, 771; also *J. pr. Chem.* 33, 427; further: *Compt. rend.* 20, 51;

also *N. J. Pharm.* 7, 129; also *Pogg.* 65, 420) that this anomaly disappears when the specific gravity of the vapour is taken at least 100° above the boiling point of acetic acid. Close above the boiling point, the density, as shewn by the following table, is even greater than it should be for a $\frac{1}{3}$-atomic vapour, or a vapour of 3 volumes. This density diminishes as the temperature rises, till, at 250°, it becomes equal to that of a diatomic gas, after which it is not altered by further rise of temperature:

Temperature	125°	130°	140°	150°	160°	171°	190°	200°	219°	230°
Density	3·20	3·12	2·90	2·75	2·48	2·42	2·30	2·22	2·17	2·09

Temperature	250°	280°	300°	338°
Density	2·08	2·08	2·08	2·08

Similarly with butyric acid, which boils at 164°. The calculated density of its vapour, supposing it to be diatomic, is 3·0505; but, according to Cahours, its density varies with the temperature as follows:

Temperature	177°	208°	228°	249°	261°	290°	310°	330°
Density	3·68	3·44	3·22	3·10	3·07	3·07	3·07	3·07

Valerianic acid behaves in a similar manner to butyric acid, but its variations are not so great. (Cahours.)

The vapour of anise-camphor, $C^{20}H^{12}O^2$, which boils at 222°, has a calculated density of 5·1301, supposing it to be diatomic. But Cahours observed the following variations:

Temperature	245°	260°	270°	325°	338°
Density	5·98	5·73	5·64	5·22	5·19

Formic acid, which boils at 99°, likewise exhibits too great a vapour-density just above its boiling point. Regarding the vapour as diatomic, the calculated density is 1·5946; but Dumas found it to vary between 2·13 and 2 14 at temperatures between 115° and 118°, and Bineau found it = 2·125 at 111°.

On the other hand, wood-spirit, alcohol, ether, fusel-oil, and most compound ethers, exhibit the density of diatomic gases just above their oiling points. (Cahours.)

3. Boiling Point.—Organic compounds are more volatile in proportion as they contain a greater number of atoms of hydrogen, and a smaller number of atoms of carbon, oxygen, and nitrogen. Of polymeric compounds, the one whose compound atom contains the smallest number of elementary atoms is always the most volatile.

The boiling compound of an organic compound is higher by x . 19° than that of another organic compound, when the former,—with an otherwise similar composition—contains x . C^2H^2 more than the latter. (Kopp.)

This is shown by the following examples:

	Boiling point.	Difference.	Calculated Diff.
$C^2H^2O^4$ = Formic acid	99°		
$C^4H^4O^4$ = Acetic acid	120°	19°	1 . 19° = 19°
$C^6H^6O^4$ = Butyric acid	164°	65°	3 . 19° = 57°
$C^{10}H^{10}O^4$ = Valerianic acid	175°	76°	4 . 19° = 76°
$C^{12}H^{12}O^4$ = Caproic acid	262°	103°	5 . 19° = 95°
$C^{16}H^{16}O^4$ = Caprylic acid	236°	137°	7 . 19° = 133°

Similarly,

	Boiling point.	Difference.	Calculated Diff.
$C^2H^4O^2$ = Wood-spirit	60°		
$C^4H^6O^2$ = Alcohol	78°	18°	1 . 19° = 19°
$C^{10}H^{12}O^2$ = Fusel-oil.....	132°	72°	4 . 19° = 76°

Comp. Schiel (*Ann. Pharm.* 43, 107); Fehling (*Ann. Pharm.* 53, 409).

Also, according to Hofmann & Muspratt (*Ann. Pharm.* 54, 16):

	Boiling point.		Boiling point.	Diff.
$C^{12}H^6$ = Benzol.....	86°	$C^{14}H^8$ = Dracyl.....	106°	20°
$C^{12}H^7N$ = Aniline.....	182°	$C^{14}H^9N$ = Toluidine....	198°	16°

Also, according to Kopp:

C H O	B.P.		C H O	B.P.		Diff.
4 6 2 Alcohol.....	78	....	10 12 2 Fusel oil	132	....	57
4 4 4 Acetic acid	118	....	10 10 4 Valerianic acid.....	175	....	57
8 8 4 Acetic ether.....	74	....	14 14 4 Acetate of Amyl	131	....	57
8 8 4 Acetic ether.....	74	....	14 14 4 Valerianic ether	131	....	57
C^4H^5I Hydriodic ether	65	....	$C^{10}H^{11}I$ Hydriodate of Amyl	122	....	57

As the second series contains $3C^2H^2$ more than the first, the difference between the boiling points should be $3 . 19 = 57°$; a result nearly identical with that which is given by observation. (Kopp.)

The same law is also approximately confirmed by comparison of the following numbers:

	C	H		Boil. pt.	Calculation.
Benzol	12	6	....	85°	85° plus.
Dracyl	14	8	....	106°	1 . 19 = 104°
Cumol	18	12	....	153°	3 . 19 = 142°
Cymol	20	14	....	175°	4 . 19 = 161°
Oil of Copaiba....	30	24	....	260°	9 . 19 = 256°

The following are less accordant:

	C	H		Boil. pt.	Calculation.
Amylene	10	10	....	39°	39° plus.
Oleene	12	12	....	55°	1 . 19 = 58°
Elaene	16	16?	....	110°	3 . 19 = 96°
Paramylene	20	20	....	160°	5 . 19 = 134°
Cetene	32	32	....	275°	11 . 19 = 248°

In these compounds, the addition of C^2H^2 appears to raise the boiling point more than 19°; hence Schröder assumes 26° as the real increment; this however is too great, in the case of cetene, for example.

If the number 19 were correct in all cases, the difference between a member of the ethylene-series and a corresponding member of the amylene-series would always be $3 . 19 = 57°$, because the members of the latter series differ from those of the former, only by containing $3C^2H^2$ in addition. But the difference of temperature is often greater, and varies in different members:

Ethylene series.	Boiling pt.	Amylene series.	Boiling pt.	Diff.
$C^4H^4O^2$	22°	$C^{10}H^{10}O^2$	96°	74°
C^4H^5Cl	11°	$C^{10}H^{11}Cl$	102°	91°
$C^4H^6S^2$	36°	$C^{10}H^{12}S^2$	117°	81°
C^4H^5O,NO^3	16°	$C^{10}H^{11}O,NO^3$	96°	74°

This law, discovered by Kopp, that the addition of C^2H^2 raises the boiling point of a compound by about 19°, is confirmed in a variety of ways. Since, however, in the comparison of certain compounds, this

number is not found to be exact, Schröder supposes that in many compounds, as in the ethylic and methylic ethers, the influence of C^2H^2 on the boiling point amounts to about 16°, and in the acids to 21°. Kopp attributes these discrepancies to want of accuracy in determining the boiling points of the compared compounds. For in the greater number of instances, the conditions for exact determination of the boiling points were not observed, such as constant atmospheric pressure corresponding to 0·76 metr., the introduction of platinum wire into the liquid, and the immersion of the thermometer in the vessel, so that the stem may be completely surrounded with vapour, the vapour being allowed to escape by a tube passing through the cork. (For further observations on this matter, *vid.* Kopp, *Chem. Soc. Q. J.* 3, 104.)

In compounds consisting wholly of carbon and hydrogen, each additional double atom of carbon which enters, raises the boiling point by a quantity varying from 35° to 35·5°, and each double atom of hydrogen lowers it by 15°. (Gerhardt.) This agrees very nearly with Kopp's supposition that each addition of C^2H^2 raises the boiling point 19°; for 35−15=20.

In calculating the boiling points of these compounds, we may start from oil of turpentine. To find from this the boiling point of another hydro-carbon of known composition, it is necessary first to determine the difference of C^2 and H^2. As many times as the compound in question contains C^2, more or less than oil of turpentine, so many times 35° must be added to or subtracted from the boiling point of oil of turpentine; and, as many times as the compound contains H^2 more or less, so many times 15° must be taken from or added to the boiling point.

Thus, Cymene, $C^{20}H^{14}$, contains 2H less than oil of turpentine, whence its boiling point should be 15° higher; now 160°+15°=175°. (Observation gives in fact 175°.)—Cumene, $C^{18}H^{12}$, contains 2C and 4H less than oil of turpentine; 160−35+2 . 15=154. (Observation gives 153°.)—Naphthalin, $C^{20}H^8$, contains 8H less than oil of turpentine; 160+4 . 15=220. (Observation gives 221°.) Styrol, $C^{16}H^8$ contains 4C and 8H less than oil of turpentine, 160−2 . 35+4 . 15=150°. (Observation gives 146°.)

In those cases in which this mode of calculation does not give the boiling point correctly, the difference may arise partly from impurity in the hydrocarbon whose boiling point was determined (as, for example, when it contains a small quantity of an oxidized hydrocarbon, which raises the boiling point), partly from the fact that many hydrocarbons are altered by ebullition, in such a manner that their boiling points are raised,—and partly from want of due care in determining the boiling point. (Gerhardt, *N. Ann. Chim. Phys.* 14, 107; also *J. pr. Chem.* 35, 300.—*Compt. rend. mensuels*, 1, 77.)

A compound which contains C^4H^2 more than another, boils 52° higher. (Schröder.) According to Gerhardt's law, the difference should be 55°; for 2 . 35−15=55.

			B. P.	Diff.
Cinnamic acid	$C^{18}H^8O^4$	....	293°	54°
Benzoic acid	$C^{14}H^6O^4$	....	239°	
Cinnamic ether	$C^{22}H^{12}O^4$	....	260°	51°
Benzoic ether	$C^{18}H^{10}O^4$	....	209°	
Cinnamene	$C^{16}H^8$	....	140°	54°
Benzol	$C^{12}H^6$	....	86°	

A compound which differs from another by the addition of C^2O^4, has a boiling point 91° higher. (Schröder.)

			B. P.	Diff.
Carbonic ether	$2(C^4H^5O),C^2O^4$	$= C^{10}H^{10}O^6$	126°	91°
Ether	$C^8H^{10}O^2$	$= C^8H^{10}O^2$	35°	
Succinic ether	$2(C^4H^5O),C^8H^4O^6$	$= C^{16}H^{14}O^8$	214°	91°
Acetate of Amyl	$C^{10}H^{11}O,C^4H^3O^3$	$= C^{14}H^{14}O^4$	125°	
Benzoate of methyl	$C^2H^3O,C^{14}H^5O^3$	$= C^{16}H^8O^4$	198°	92°
Dracyl	$C^{14}H^8$	$= C^{14}H^8$	106°	

The boiling point of an acid is 40° higher than that of the corresponding alcohol, which differs from the acid by containing 2H more and 2O less. (Kopp.)

		B. P.			B. P.
Formic acid	$C^2H^2O^4$	99°	Acetic acid	$C^4H^4O^4$	120°
Wood-spirit	$C^2H^4O^2$	60°	Alcohol	$C^4H^6O^2$	78°
		39°			42°

		B. P.
Valerianic acid	$C^{10}H^{10}O^4$	175°
Fusel-oil	$C^{10}H^{12}O^2$	132°
		43°

The same difference of 40° is found between cuminol, $C^{20}H^{12}O^2$, which boils at 220°, and camphogene, $C^{20}H^{14}$, which boils at 175°; also between acetic ether $C^6H^8O^4$, which boils at 74°, and common ether, $C^8H^{10}O^2$, which boils at 35°, the first of each of these pairs of substances containing 2O more and 2H less than the second. (Schröder.)

The boiling point of an acid is 63° higher than that of the ether which it forms with wood-spirit, and 44° higher than that of the ether which it forms with alcohol. (Reickher, *Ann. Pharm.* 46, 222; Kopp.)

	B. P. of the free acid.	B. P. of its methyl-ether.	Diff.	B. P. of its ethyl-ether.	Diff.
Formic acid	99°	37°	62°	55°	44°
Acetic acid	120	56	64	74	46
Butyric acid	164	102	62	110	54
Valerianic acid	175	114	61	133	42
Oxalic acid	216	161	55	183	33
Succinic acid	235	198	37	214	21
Benzoic acid	239	198	41	209	30
Cinnamic acid	293	241	52	260	33

These numbers certainly exhibit a few great discrepancies, but only with regard to those acids whose boiling points are high, and therefore difficult to determine with exactness.

Compound ethers which are metameric with each other, have equal boiling points. (Kopp.)

Thus, acetate of methyl, $C^2H^3O,C^4H^3O^3$, boils at 55·7°; formiate of ethyl, C^4H^5O,C^2HO^3, at 55·5°; formiate of amyl, $C^{10}H^{11}O,C^2HO^3$, at 116°; and valerate of methyl, $C^2H^3O,C^{10}H^9O^3$, at 114°; acetate of amyl, $C^{10}H^{11}O,C^4H^3O^3$, at 133·3°, and valerate of ethyl, $C^4H^5O,C^{10}H^9O^3$, at 133·2°.

The boiling point of an acid is 81° higher than that of a compound

ether which is metameric with it, though the vapours of both compounds are diatomic. (Kopp.)

			B. P.	Diff.
Acetic acid	C^4H^4O	....	120°	83°
Formiate of methyl	C^2H^3O,C^2HO^3	....	37°	
Butyric acid	$C^8H^8O^4$	....	164°	90°
Acetate of ethyl	$C^4H^5O,C^4H^3O^3$	....	74°	
Valeric acid	$C^{10}H^{10}O^4$	....	175°	73°
Butyrate of methyl	$C^2H^3O,C^8H^7O^3$	....	102°	

Schröder (*Pogg.* 62, 184 and 337, more fully in a special work, Mannh. 1844) imagines organic compounds to be composed of hydrogen and certain binary compounds which he calls *Components*. Each of these components exerts a determinate influence on the boiling point either to raise or to depress it.

H^2, *Bihydrogen*, lowers the boiling point, by 3°. All other components raise the boiling point; H^2O^2, *water of hydration*, by 113·5°; C^2O^2, *carbonic oxide*, by 57°; C^2O^4, *carbonic acid*, by 90°; *formyl*, by 52°; C^2H^2, in the form of *methylene*, by 21°, and C^2H^2 in the form of *elayl*, by 17°.

To calculate the boiling point of any compound, we may set out from Benzol $= C^{12}H^6$ ($= 3 : C^4H^2 = Triformyl$). Since this compound boils at 86°, and moreover 3 . C^4H^2 must raise the boiling point by 3 . 52 = 156°, the influence of the triformyl = 156° must be deducted from the boiling point 86°, leaving − 70°; and to this − 70°, must be added the influence of the components of the compound whose boiling point is sought. If, for example, the compound is Caoutchin = C^8H^8, consisting of 4 At. methylene, we must add 4 . 21 = 84 to the − 70°, which makes the boiling point of caoutchin = 14° (by observation it is 14·5). Similarly, alcohol = bihydrate of elayl = $2C^2H^2 + H^2O^2$; therefore, 2 . 17 + 113·5 = 147·5; 147·5 − 70° = + 77·5° = boiling point of alcohol (by observation, 78°).

Hence, to find the boiling point of an organic compound, we must resolve it, in the most convenient manner, into its components, estimate their aggregate effect upon the boiling point, and diminish the sum by 70°.

The table calculated by this method gives results agreeing very closely with observation; it must not, however, be forgotten that, as occasion requires, C^2H^2 is sometimes introduced as methylene, with an influence of 21°, sometimes as elayl with an influence of 17°, sometimes even in both capacities in the same compound; thus, fusel-oil, $C^{10}H^{12}O^2$, is regarded as a compound of C^2H^2 in the form of methylene, $4C^2H^2$ in the form of elayl, and H^2O^2, while valerianic acid, $C^{10}H^{10}O^4$, a compound intimately related to it, is supposed to consist of 2 methylene and 2 elayl with C^2O^2 and H^2O^2. Nevertheless, it is not with all compounds that this method yields satisfactory results. For instance, aldehyde, $C^4H^4O^2$, may be regarded either as $C^4H^2 + H^2O^2$, in which case the calculation will be: 52° + 113·5° − 70° = + 95·5°,—or as $C^2O^2 + C^2H^2 + H^2$, which gives 57 + 21 − 3 − 70 = + 5°. Thus, the calculation gives for the boiling point of aldehyde, either 95·5° or 5°, whereas the actual boiling point is 21°. In a similar manner, acetone gives either too high or too low a point, according to the components of which it is supposed to be formed. Nevertheless, the agreement which exists in many cases, induces the supposition that this theory has some foundation in fact, and so far would

still hold good, even if organic compounds were not supposed to be made up of the components above mentioned.

From the uncertain results obtained by assuming the existence of these components, Schröder has lately been induced to transfer their supposed influence on the boiling point to their elements. According to this latter view, each double atom of hydrogen (H^2) lowers the boiling point of a componnd 10°; each double atom of carbon (C^2) raises it 30°; and each double atom of oxygen (O°), 29°. The sum of these influences, diminished as before by 70°, gives the boiling point.

This latter theory approximates in many points to the preceding. According to the former, H^2 lowers the boiling point by 3°; according to the latter, by 10°; according to the former, C^2O^2 raises it by 57°; according to the latter, C^2 gives 31 and O^2 29, together=60°; according to the former, C^2O^4 raises the boiling point by 90°; according to the latter view, C^2 raises it by 31, and $2O^2$ by 58, the sum of which is 89°; according to the former, C^4H^2 raises it by 52°; according to the latter, $2C^2$ raises it by 62°, and H^2 by −10, the sum of which is 52°; according to the former theory, C^2H^2 raises it, sometimes by 16° sometimes by 21°; according to the latter by (31 −10) or 21°. In H^2O^2, however, there is a remarkable difference, inasmuch as, according to the former theory, it raised the boiling point 113·5°, whereas, according to the latter, the increase which it produces is only 29°−10°=19°; and hence, perhaps, it chiefly arises that with regard to the greater number of compounds, the latter theory gives less satisfactory results than the former. With the hydrocarbons, the numbers obtained are satisfactory. Thus, Benzol, $C^{12}H^6$, which boils at 86°, gives (6 . 31−3 . 10−70), which is actually equal to 86°; Dracyl, $C^{14}H^8$, which boils at 106°, gives (7 . 31−4 . 10−70) equal to 107°; and Cetene $C^{32}H^{32}$, which boils at 275°, gives (16 . 31−16 . 10−70) or 276°.—But in most oxygen-compounds, the calculated results differ widely from those of observation. It is true that ether, $C^8H^{10}O^2$, which boils at 35°, gives a satisfactory result: $4C^2=4 . 31=124$; $O^2=29$; $5H^2=-50$; 124+29 − 50=103; 103−70=33. But with formic acid, which boils at 99°, calculation places the boiling point at 11°, that is to say, 88° too low; and similarly, in the greater number of oxygen-compounds, the calculated boiling point is much lower (sometimes by more than 100°) than that which is given by observation. Schröder supposes that, in certain compounds containing oxygen, this element sometimes exerts twice, and sometimes four times as great an influence as in certain others, *i. e.*, that O^2 frequently raises the boiling point by 58° or 116°, instead of only 29°.

According to Löwig (*Pogg.* 66, 250), 1 At. H lowers the boiling point of a compound by 29·2°; 1 At. C raises it by 38·4°; and 1 At. O either raises it by 28° or lowers it by 8·4°, according to the greater or less condensation of the O-volume in the compound. The sum thus obtained is not to be diminished by 70° or any other number, &c.—According to this theory, marsh-gas should boil at −40° or −20°, accordingly as it is regarded as C^2H^4 or CH^2. (2 . 38·4 − 4 · 29·2= − 40; or, 38·4 − 2 . 29·2= − 20). Benzol, $C^{12}H^6$, should boil at 285·6° instead of 86° (12 . 38·4 − 6 . 29·2=285·6), &c. *Comp.* Schröder (*Pogg.* 66, 250).

The boiling point question has hitherto been treated exclusively according to the radical-theory, and not according to the nucleus-theory. It is, therefore, a question whether the latter may not afford a further

clue to its solution, and whether, by assigning to the hydrogen and oxygen within the nucleus a different amount of influence from that which is exerted by the same elements without the nucleus, we may not succeed in discovering a *universal* law. That this circumstance is of importance may be seen from the following facts: Salicylous acid and benzoic acid have the same empirical formula $=C^{14}H^6O^4$; but the former boils at 196°, the latter at 239°. The difference of 43° is too great to be attributed to error of observation, and must, together with the other striking differences in the properties of the two acids, be attributed to difference of constitution. Benzoic acid is supposed by Laurent to contain the nucleus benzene, $C^{14}H^6$, which, together with 4O externally situated, forms benzoic acid, $C^{14}H^6,O^4$; but salicylous acid is supposed to be formed upon a different primary nucleus, $C^{14}H^8$ (possibly identical with dracyl). A secondary nucleus, $C^{14}H^6O^2$, derived from this by the substitution of 2O for 2H, forms, with 2 additional atoms of oxygen, the compound $C^{14}H^6O^2,O^2$, which belongs to the aldehyde type, may be compared with bitter almond oil, $C^{14}H^6O^2$, and moreover requires the addition of 2O to convert it into an acid actually comparable with benzoic acid, viz., salicylic acid, $C^{14}H^6O^2,O^4$. It appears, then, that the circumstance of benzoic acid having 4O without the nucleus, and salicylous acid 2O within and 2O without, produces a difference of properties, and among the rest in the boiling point; moreover it seems to follow, from this example, that oxygen within the nucleus raises the boiling point less than oxygen without. In connection with this matter, we might further examine, and perhaps decide, the question, as to whether benzoic and salicylous acid should be expressed, as in Laurent's system, by the formulæ $C^{14}H^6,O^4$ and $C^{14}H^6O^2,O^2$, or, according to the principles explained on pages 30—37, by $C^{14}H^6O,HO^3$, and $C^{14}H^6O^3,HO$.

By way of example, we may take the following attempt to calculate boiling points according to the former of these two views, the results of which are tolerably satisfactory. The boiling point of the C and H in the nucleus is first determined according to Gerhardt's method (p. 57). It is further empirically assumed, from calculations of the boiling points of different compounds, that O^2 within the nucleus raises the boiling point 25°; that the first O^2 without the nucleus raises it 50° (in some rare cases, as in that of phenic acid, the rise thereby produced amounts to 100°); and that the following O^2 without the nucleus raises it 100° (rarely, as in benzoic acid, only 50°). H^2O^2 without the nucleus raises the boiling point 108°. The observed boiling point is placed in brackets before the calculated value:

Formic acid, $C^2H^2+O^4$	Wood-spirit, $C^2H^3+H^2O^2$	Acetic acid, $C^4H^4+O^4$
C^2H^2 — 50°	C^2H^2 — 50°	C^4H^4 — 30°
O^2 without — 50°	H^2O^2 +108°	O^2 without + 50°
O^2 without +100°	(60°) + 58°	O^2 without +100°
(99°) +100°		(120°) +120°

Alcohol, $C^4H^4+H^2O^2$	Aldehyde, $C^4H^4+O^2$	Butyric acid, $C^8H^8+O^4$
C^4H^4 — 30°	C^4H^4 —30°	C^8H + 10°
H^2O^2 +108°	O^2 without +50°	O^2 without + 50°
(78°) +78°	(21°) +26°	O^2 without +100°
		(164°) +160°

Valerianic acid, $C^{10}H^{10} + O^4$

$C^{10}H^{10}$	30°
O^2 without	50°
O^2 without	100°
(178°)	180°

Fusel-oil, $C^{10}H^{10} + H^2O^2$

$C^{10}H^{10}$	30°
H^2O^2	108°
(132°)	138°

Caproic acid, $C^{12}H^{12} + O^4$

$C^{12}H^{12}$	50°
O^2 without	50°
O^2 without	100°
(202°)	200°

Caprylic acid, $C^{16}H^{16} + O^4$

$C^{16}H^{16}$	90°
O^2 without	50°
O^2 without	100°
(236°)	240°

Lactone, $C^{10}H^8O^2 + O^2$

$C^{10}H^8$	45°
O^2 within	25°
O^2 without	50°
(92°)	120°

Metacetone, $C^{10}H^{10} + O^2$

$C^{10}H^{10}$	30°
O^2 without	50°
(84°)	80°

Mesitic-ether, $C^{12}H^{10} + O^2$

$C^{12}H^{10}$	65°
O^2 without	50°
(120°)	115°

Acrolein, $C^6H^4 + O^2$

C^6H^4	5°
O^2 without	50°
(52°)	55°

Acrylic acid, $C^6H^4 + O^4$

C^6H^4	5°
O without	50°
O^2 without	100°
(above 100°)	155°

Pyrogallic acid, $C^{12}H^6O^2 + O^4$

$C^{12}H^6$	95°
O^2 within	25°
O^4 without	100°
(210°)	220°

Phenic acid, $C^{12}H^6 + O^2$

$C^{12}H^6$	95°
O^2 without	100°
(188°)	195°

Salicylous acid, $C^{14}H^6O^2 + O^2$

$C^{14}H^6$	130°
O^2 within	25°
O^2 without	50°
(196°)	205°

Benzoic acid, $C^{14}H^6 + O^4$

$C^{14}H^6$	130°
O^4 without	100°
(239)	230°

Bitter almond oil, $C^{14}H^6 + O^2$

$C^{14}H^6$	130°
O^2 without	50°
(180°)	180°

Cinnamic acid, $C^{18}H^8 + O^4$

$C^{18}H^8$	185°
O^4 without	100°
(290°)	285°

Camphoric acid Anhydride, $C^{20}H^{14}O^4 + O^2$

$C^{20}H^{14}$	175°
O^4 in the nucleus	50°
O^2 without the nucleus	50°
(above 270°)	275°

Campholic acid, $C^{20}H^{18} + O^4$

$C^{20}H^{18}$	145°
O^2 without	100°
(250°)	245°

Pyroguajacic acid, $C^{14}H^8 + O^4$

$C^{14}H^8$	115°
O^2 without	100°
(210°)	215°

Cuminic acid, $C^{20}H^{12} + O^4$

$C^{20}H^{12}$	190°
O^4 without	100°
(above 250°)	290°

Pyroterebic acid, $C^{12}H^{10} + O^4$

$C^{12}H^{10}$	65°
O^2 without	50°
O^2 without	100°
(above 200)	115°

Caryophyllic acid, $C^{20}H^{12}O^2 + O^2$

$C^{20}H^{12}$	190°
O^2 within	25°
O^2 without	50°
(243°)	265°

Cumarin, $C^{18}H^6O^2 + O^2$

$C^{18}H^6$	200°
O^2 within	25°
O^2 without	50°
(270°)	275°

Anisol, $C^{14}H^8 + O^2$

$C^{14}H^8$	115°
O^2 without	50°
(above 150°)	165°

Hydranisyl, $C^{16}H^8O^2 + O^2$

$C^{16}H^8$	150°
O^2 within	25°
O^2 without	50°
(254°)	225°

Cuminol and Anise-camphor, $C^{20}H^{12}O^2$

$C^{20}H^{12}$	190°
O^2 within	25°
(220°) and (222°)	215°

Parsley-camphor, $C^{20}H^{12}O^4 + O^2$	
$C^{20}H^{12}$	190°
O^4 in the nucleus	50°
O^2 without	50°
(300°)	290°

Peppermint-camphor, $C^{20}H^{20} + O^2$	
$C^{20}H^{20}$	130°
O^2 without	50°
(213°)	180°

Common camphor, $C^{20}H^{16}O^2$	
$C^{20}H^{16}$	160°
O^2 within	25°
(204°)	185°

Or? $C^{20}H^{16} + O^2$	
$C^{20}H^{16}$	160°
O^2 without	50°
(204°)	210°

Cajeput oil, $C^{20}H^{18}O^2$	
$C^{20}H^{18}$	145°
O^2 in the nucleus	25°
(173°)	170°

Furfurol, $C^{10}H^4O^2 + O^2$	
$C^{10}H^4$	75°
O^2 within	25°
O^2 without	50°
(162°)	150°

Carvacrol, $C^{24}H^{18}O^2$	
$C^{24}H^{18}$	215°
O^2 in the nucleus	25°
(232°)	240°

But this mode of calculation, though it may appear tolerably satisfactory in so far as regards the examples in the preceding table, is nevertheless inaccurate when applied to many others; partly perhaps because the composition and boiling points of these latter have not been correctly determined, but partly also because the mode of calculating is not adapted to certain compounds, for which, perhaps, peculiar laws should be assumed. Such, for instance, is the case with methylic, ethylic, and amylic ether, with acetone and certain compounds allied to it, with lignone and its products of decomposition, &c.

But even if we should succeed, by this or any other mode of calculation, in overcoming the principal difficulties, it will still remain uncertain whether we shall ever arrive at a complete solution of the problem of determining the boiling point of an organic compound from its composition. The numerous oils composed of $C^{20}H^{16}$ have boiling points varying between 156° (terebene) and 173° (carvene); and this difference of boiling point is accompanied by difference of specific gravity, and of optical and chemical relations (*e. g.*, towards hydrochloric acid gas). We cannot, therefore, ascribe these deviations merely to impurity in the oils or to errors of observation, but are forced to admit that in the same nucleus, the 20C and 16H may be united in different ways; and as this difference of arrangement and the influence which it exerts on the boiling point are likely to remain unknown, the calculation of the boiling point, even if founded on the most accurate data, cannot be expected to give an exact result in all cases.

Certain other compounds likewise have different boiling points, though their composition is the same, *e. g.*, maleic and fumaric acids; there are, however, other reasons which seem to show that the boiling point of fumaric acid should be doubled.

Some facts seem to show that nitrogen raises the boiling point of a compound much more than carbon or oxygen, and that 1N introduced in the place of 1H produces a rise of about 100°. Thus, benzol, $C^{12}H^6$, boils at 86°; the compound $C^{12}H^8$ boils at a still lower temperature; but the boiling point of aniline, $C^{12}H^7N$, is 182°; Elaene (probably $C^{16}H^{16}$) boils at 110°; coniine, $C^{16}H^{15}N$, at 212°. This strong fixing power of nitrogen and oxygen in organic compounds is very remarkable, when considered in relation to their otherwise great elasticity.

4. Relations to Light. — *Colour.*—Most organic compounds are colourless, even those which contain the greatest number of carbon-atoms; some, which however contain at least 14 At. carbon, viz., the *organic colouring matters*, are brightly coloured, not only in the free state, but likewise in most of their compounds with colourless substances.

The *Refracting Power* of organic liquids is greater in proportion as they are specifically heavier and more viscid; in the hydrocarbons, it is greater as the quantity of carbon exceeds that of the hydrogen, and in oxygenated compounds, it increases as the quantity of oxygen is proportionally less. If two or more isomeric, polymeric, or metameric compounds, have the same density and consistence, they exhibit the same refracting power; in the contrary case, the denser or more viscid compound has the greater refracting power.

For more exact information on this point *vid.* Becquerel & Cahours (*Compt. rend.* 11, 876; also *Pogg.* 51, 427; also *J. pr. Chem.* 23, 129); and Deville (*Compt. rend.* 11, 865; also *J. pr. Chem.* i. 3, 134).

Circular Polarization.—Certain colourless or very slightly coloured organic liquids, such as oil of turpentine, or solutions of certain solid substances in water, or in other liquids which have no specific action of their own — *e. g.*, the aqueous solutions of tartaric acid, dextrin, the various kinds of sugar, and several natural alkaloids,—exhibit, as discovered by Biot, a peculiar relation towards polarized light transmitted through them; they exert, in fact, a *Rotatory Power* upon it, turning it, according to their peculiar nature, to the right or to the left; in other words, they produce *Circular Polarization*, or a *Rotation* or *Turning of the plane of Polarization* to the right or to the left. Any given liquid always produces a rotation of the same number of degrees, provided the concentration of the liquid and the thickness of the stratum through which the polarized light has to pass, remain the same; if the thickness of the stratum or the degree of concentration be increased, the angle of rotation likewise increases. Now, since most other liquids, and most solid substances, when dissolved in water, alcohol, &c., exert no action whatever on polarized light, it follows that the presence of tartaric acid, sugar, &c., in liquids, may be discovered by means of circular polarization. Moreover, substances in the liquid state may, by the same means, be distinguished one from the other, either by one producing rotation and the other none,—*e. g.*, tartaric and racemic acid; or one producing a rotation to the right and the other to the left; or by one producing a greater rotation than the other, with equal concentration and equal thickness of the liquid. When the nature of a dissolved substance is known, and the thickness of the liquid stratum likewise given, the concentration of the solution may be calculated from the amount of the rotation. It is even possible, by examining this property, to discover differences between two compounds, which, in regard to their other properties and chemical relations, must be regarded as identical, *e. g.*, certain kinds of oil of turpentine and of sugar in various isomeric states, in which they either produce rotation to the right or to the left; or none at all.

Biot, *Ann. Chim. Phys.* 52, 58; also *Schw.* 68, 151; also *Pogg.* 28, 165; also *Ann. Pharm.* 7, 257; *Ann. Chim. Phys.* 64, 401; 69, 22.—*N. Ann. Chim. Phys.* 10, 11.—*Compt. rend.* 15, 528 and 619; 21, 1.—*N. J. Pharm.* 4, 350.

¶ A very remarkable relation between rotatory power and molecular constitution has been discovered by Pasteur (*N. Ann. Ch. Phys.* 28, 56; abstr. *Chem. Soc. Qu. J.* 3, 79). It has been long known that tartaric acid and its salts turn the plane of polarization to the right, whereas racemic acid and the racemates, which are isomeric with them, possess no such property. Now, Pasteur has shown that racemic acid is a compound of two other acids, identical in chemical composition, crystallizing in forms which present the same number of perfectly similar faces, but are disposed *symmetrically* with respect to each other (like the image and object in a mirror, or the two halves of the human body), and therefore incapable of coinciding by superposition. These crystals are in fact rectangular prisms, having their lateral edges replaced by planes; and the intersection of *two* only of these planes with the terminal faces of the prism are replaced by facets; hence the crystals are hemihedral. Now one of these acids turns the plane of polarization to the right, and the other to the left: they are called respectively, *Dextroracemic* and *Lævoracemic* acids, the former being that which is usually called tartaric acid. A solution containing equal weights of the two acids yields, on evaporation, crystals of racemic acid, perfectly homohedral, and having no action whatever on polarized light. The relations of form and rotatory power which exist in the acids themselves, are likewise found to the fullest extent in their salts. All the chemical properties of the tartrates or dextroracemates are reproduced, in the minutest details, in the lævoracemates; and to each tartrate there corresponds a lævoracemate, differing from the former in nothing but the symmetrical situation of certain corresponding faces of the crystals and the direction of the rotatory power.—Pasteur has also shown (*N. Ann. Chim. Phys.* 34, 30) that aspartic acid prepared from fumarate of ammonia (a substance not possessing rotatory power), is itself without action on polarized light, although the same acid, when prepared in the ordinary way from asparagine, possesses the rotatory power; moreover, that inactive aspartic acid may be converted into an inactive malic acid by the same process as that by which active aspartic acid is converted into active malic acid. These active and inactive acids are exactly alike in all their chemical properties, and form salts identical in every respect, excepting that in some few instances the crystals of the two varieties belong to different systems, and that the active substances always exhibit hemihedral facets, which the inactive compounds never do. It does not appear, however, that the inactive varieties of aspartic and malic acid can be resolved into two oppositely active compounds like dextroracemic and lævoracemic acid; but it is highly probable that there exists an inactive variety of malic acid and also of asparagine. ¶

The apparatus employed by Ventzke (*J. pr. Chem.* 25, 65) for the observation of circular polarization, is constructed as follows: A metal tube lying horizontally is connected at each end with a Nichol's prism. The prism at the further end is immoveable, and directed towards the brightest part of an Argand lamp; but the prism at the nearer end, through which the eye is directed to the light, is capable of turning round the axis of the tube, and is provided with an index which moves upon a graduated disc surrounding the nearer end of the tube, and marked 0° at its highest, and 180° at its lowest point. If now the eye be directed through the empty tube, towards the Argand lamp or towards the solar light, and the nearer prism turned once round, two points are found,

defined with considerable sharpness, at which the whole of the light disappears. The index is fixed in such a manner as to point to 0° and 180° at the two points at which perfect darkness is produced. A glass tube, 0·234 met. long, closed at each end with a glass plate, and completely filled with the liquid to be examined, is now introduced into the metal tube, so that the rays of the lamp may pass, first through the further prism, then through the stratum of liquid 0·234 met. long, and then through the nearer prism, into the eye. If the liquid, water for example, has no rotatory power, perfect darkness is produced as before, when the index points to 0°; but, if the liquid possesses rotatory power, the light of the lamp is still seen with the prism in that position. But, if the nearer prism, with its index, be turned round to the right, then if the liquid turns the plane of polarization to the right, the following colours appear in succession: light blue, dark blue, violet, purple, red, orange; if, on the contrary, the polarization is to the left, the same series of colours is exhibited on turning the prism in that direction. In either case, the rotation is to be stopped as soon as the red, intermediate between the purple and orange, appears, and the number of degrees from 0°, which the index then marks, is to be read off. This is the number of degrees of circular polarization which the liquid exhibits, either to the right or to the left.

5. Physiological Relations.—All volatile organic compounds are odoriferous, and most of them are distinguished by very strong odours; *e. g.*, volatile acids, volatile oils, camphors or stearoptenes, and alcoholic liquids; marsh gas and olefiant gas have but very little odour.

Some organic compounds, as gum, starch, woody fibre, white of egg, &c., have no *Taste;* others have a sour taste (most acids); or a rough taste (tannin); or sweet (sugar, glycerin, glycocol); or bitter (bitter principles, narcotic substances, and many acrid substances, also many resins); or acrid (acrid oils and camphors, acrid resins, acrid alkaloids); or fiery (alcoholic liquids, volatile oils, camphors).

In their medicinal action on the body, organic compounds likewise exhibit the greatest differences; and it is a matter of the greatest wonder, that the same elements, according to the proportion in which they enter into an organic compound, should produce, sometimes nutritious matters, sometimes medicinal substances and poisons, sometimes indigestible and inert substances.

Difference of Properties accompanied with apparently similar Constitution.

There are many organic compounds which, though possessing the same per-centage composition, nevertheless exhibit marked differences in their physical and chemical relations. These differences may be ascribed to Isomerism, Polymerism, and Metamerism. (I., 108–111.)

Isomerism.

Many volatile oils have a composition expressed by the formula $C^{20}H^{16}$, but differ in specific gravity, boiling point, circular polarization, smell, and taste,—in the quantity of hydrochloric acid gas which they are able to absorb, and in the liquid or solid nature of the resulting

hydrochlorate,—also in their power of dissolving caoutchouc, &c. Thus, oil of turpentine is composed of two such isomeric oils, and these may be transformed into other isomeric modifications. The same formula, $C^{20}H^{16}$, likewise belongs to the following oils: Oil of Lemons (boiling point 146°); neutral oil of Cloves (Sp. gr. 0·918; B. P. 142°); oil of Elemi-resin (Sp. gr. 0·852; B. P. 166°); Carvene (B. P. 173°); and several others.

Crystalline Eugenin, and acid oil of cloves (caryophyllic acid), have the same formula, $C^{20}H^{12}O^4$.

Oil of Cumin, Esdragon-oil, Fennel-oil, and Anise-camphor are composed of $C^{20}H^{12}O^2$, and may be converted by treatment with oil of vitriol, chloride of zinc, &c., into three other oily, camphor-like, or resinous isomeric compounds.

The formula of Itaconic acid is $C^{10}H^6O^8$, the same as that of Citraconic acid; but the salts of these acids exhibit different properties.

Tartaric and Racemic acid $= C^8H^6O^{12}$, are likewise isomeric. Not only are the compounds of these acids with water and with bases different in their properties, but tartaric acid in the state of aqueous solution exhibits circular polarization, while racemic acid does not.

Mucic acid, $C^{12}H^{10}O^{16}$, which is insoluble in alcohol, is converted, by boiling its aqueous solution, into the isomeric substance, Paramucic acid, which is soluble in alcohol; both these acids are isomeric with Saccharic acid.

To the same class of bodies appear to belong: Pyromucic and Pyromeconic acid $= C^{10}H^4O^6$;—Ampelic and Salicylic acid $= C^{14}H^6O^6$;—Ethalic and Palmitic acid $= C^{32}H^{32}O^4$;—Oleic and Elaidic acid $= C^{36}H^{34}O^4$;—Pinic and Sylvic acid $= C^{40}H^{30}O^4$.

Furfuramide and Furfurine are both composed of $C^{30}H^{12}N^2O^6$. The former, when treated with acids, is resolved into an ammoniacal salt and furfurol; and, by contact with aqueous potash, it is converted into the isomeric compound, furfurine, which is not decomposed by acids, but is a salifiable base uniting with acids to form salts.

Salicylous acid is: $C^{14}H^6O^3,O^2$, and Benzoic acid, $C^{14}H^6,O^4$.

Crystalline Eugenin and Pyroguaiacic acid, an oily substance quite different from it, both have the formula $C^{14}H^8O^4$; the former is probably $C^{14}H^6O^2,H^2O^2$; the latter, $C^{14}H^8,O^4$.

Gum arabic, dextrin, milk-sugar, starch, and woody fibre, when well dried *per se*, all have the formula $C^{12}H^{10}O^{10}$, or $C^{24}H^{20}O^{20}$. This is perhaps a case of polymerism, one compound being $C^{12}H^{10}O^{10}$, another $2(C^{12}H^{10}O^{10})$, &c.

Butyrone and Oenanthol are $C^{14}H^{14}O^2$.

Metacetone and Valeral are $C^{10}H^{10}O^2$.—This case may, however, be ascribed to metamerism, if metacetone be regarded as a compound of the second order $= C^6H^6O^2,C^4H^4$ (p. 44). This view of its composition is supported by the fact that metacetone is converted by chromic acid, not into valerianic acid, but into metacetonic acid, $C^6H^6O^4$, and acetic acid, $C^4H^4O^4$.—Similar remarks apply to the preceding case.

These phenomena of isomerism are very probably due to differences in the arrangement of the atoms.

Polymerism.

Polymeric substances are supposed to differ from one another in this manner, that the atom of one body contains a larger number of

simple atoms than that of another; *e. g.*, the atom of one compound containing 1 . ($C^2H^7O^2$), that of another contains 2 . ($C^2H^7O^2$), that of a third, 3 . ($C^2H^7O^2$), and that of a fourth, 4 . ($C^2H^7O^2$), &c. This hypothesis is, in many cases justified by the mode of formation, the boiling point, and vapour-density of such compounds. Since, for example, sulphuric acid converts alcohol, $C^4H^6O^2$, by the abstraction of H^2O^2, into olefiant gas, the latter may be supposed to consist of C^4H^4; and similarly, cetene, which is produced from ethal, $C^{32}H^{34}O^2$, by the action of phosphoric acid, may be regarded as $C^{32}H^{32}$. Moreover, since the boiling point of a compound rises, according to a fixed law, with the number of simple atoms of the same kind which its compound atom contains (pp. 55—63), this circumstance evidently furnishes a datum for determining how many times the number of atoms of the more volatile compound must be multiplied, to give that of the more fixed compound. Finally, since the vapour-density of the most volatile of the empyreumatic oils obtained from oil-gas is twice as great as that of olefiant gas, C^4H^4, the former is supposed to contain twice as many elementary atoms as the latter, viz., C^8H^8, so that its vapour may likewise be diatomic.

Very many compounds consist of carbon and hydrogen in equal numbers of atoms, consequently 6 pts. C to 1 pt. H, or 85·714 per cent. C to 14·286 H. To this class belong: Methylene-gas (palene), C^2H^2; Olefiant gas (ethylene), C^4H^4; Faraday's most volatile oil from oil-gas, C^5H^5; Amylene, $C^{10}H^{10}$; Oleene, $C^{12}H^{12}$; Naphthene (from rock-oil) and Elaene, $C^{16}H^{16}$; Paramylene, $C^{20}H^{20}$; Cetene, $C^{32}H^{32}$. To the same category likewise belong Caoutchin, Oil of Wine, Wine-camphor, Rose-camphor, Aurad, Hatchettin, Ozokerite, and Caoutchouc, respecting which, however, there is a want of data for determining the number of atoms of which the compound atoms are formed.—When Fusel-oil, $C^{10}H^{12}O^2$, is distilled with anhydrous phosphoric acid, the first product distillate obtained is Amylene, which boils at 39°; then Paramylen, $C^{20}H^{20}$, which boils at 160°, and has a double vapour-density; and lastly, at a still higher temperature, an oil of nearly fourfold vapour-density, probably therefore $=C^{40}H^{40}$.

3 At. carbon to 1 At. hydrogen, or 18 pts. C to 1 H, or 94·74 per cent. C to 5·26 H, are found in Chrysene, $C^{21}H^9$, and in Idrialin, $C^{30}H^{10}$.

The proportion of 5 At. C to 2 At. H is found in Naphthaline, $C^{20}H^8$, Anthracene, $C^{30}H^{12}$, and Pyrene.

Cyanogen is C^2N; Paracyanogen, into which the cyanogen of cyanide of mercury is partly converted by heat, is probably C^6N^3.

Cyanic acid is C^2NHO^2; Cyanuric acid is probably $C^6N^3H^3O^6$; moreover, the insoluble cyanuric acid has the same composition per cent.

Volatile Chloride of Cyanogen is C^2NCl; the fixed chloride is probably $C^6N^3Cl^3$.

Gaseous Methyl-ether is C^2H^3O; Alcohol is $C^4H^6O^2$.

Aldehyde, $C^4H^4O^2$, when preserved, is occasionally converted into crystals which are sometimes fusible, sometimes infusible. These two kinds of crystals are probably $C^8H^8O^4$ and $G^{12}H^{12}O^6$.

Bitter almond oil, $C^{14}H^6O^2$, when kept for some time in contact with hydrate of potash, is converted into Benzoin, $C^{28}H^{12}O^4$.

Acrolein and Mesitaldehyde, which differ greatly in their properties, both have the formula $C^6H^4O^2$; but the latter, which is much the less volatile of the two, is perhaps more correctly represented by the formula $C^{12}H^8O^4$.

Maleic, Fumaric, and Aconitic acids may be expressed by the formula,

$C^4H^2O^4$; but, judging from their different degrees of volatility, maleic acid is probably $C^4H^2O^4$, fumaric, $C^8H^4O^8$, and aconitic, $C^{12}H^6O^{12}$.

Monobasic Angelicic acid is $C^{10}H^8O^4$, and bibasic Camphoric acid, $C^{20}H^{16}O^8$.

Metamerism.

1. When two organic compounds come together, a more complex substance is often formed, containing the same number of atoms C, H, and O, as another product formed from two other organic compounds.

Formic ether is metameric with acetic methyl-ether (acetate of methyl).

	C	H	O
Alcohol — 1 Water = $C^4H^6O^2$ — HO =	4	5	1
with Formic acid — 1 Water = $C^2H^2O^4$ — HO =	2	1	3
forms Formic ether =	6	6	4
Wood-spirit — 1 Water = $C^2H^4O^2$ — HO =	2	3	1
with Acetic acid — 1 Water = $C^4H^4O^4$ — HO =	4	3	3
forms Acetic methyl-ether =	6	6	4

Similarly, Anisic methyl-ether (anisate of methyl) = $C^2H^3O,C^{16}H^7O^5$ contains the same number of atoms as Salicylic ether (salicylate of ethyl) = $C^4H^5O,C^{14}H^5O^5$. [Other examples of this kind will be found in 2.]

2. An atom of a complex organic compound may contain the same number of atoms of the several elements as 1 or 2 atoms of a primary organic compound.

Cyanate of ammonia, NH^3,C^2NHO^2, has the same number of atoms as Urea, $C^2H^4N^2O^2$.

Oxalate of methyl, C^2H^3O,C^2O^3 (or $C^4H^6O^3,C^4O^6$) = Succinic acid, $C^4H^3O^4$ (or $C^8H^3O^8$).

Formiate of methyl, C^2H^3O,C^2HO^3 = Acetic acid, $C^4H^4O^4$.

Formiate of ethyl, C^4H^5O,C^2HO^3, and Acetate of methyl, $C^2H^3O,C^4H^3O^3$ = Propionic acid, $C^6H^6O^4$.

Acetate of ethyl, $C^4H^5O,C^4H^3O^3$ = Butyric acid, $C^8H^8O^4$ = 2 Aldehyde, $2(C^4H^4O^2)$; and Chloracetic ether, $C^4Cl^5O,C^4Cl^3O^3$ = 2 Chlor-aldehyde, $2(C^4Cl^4O^2)$.

Valerate of amyl, $C^{10}H^{11}O,C^{10}H^9O^3$ = 2 Valeral, $2(C^{10}H^{10}O^2)$.

Butyrate of methyl, $C^2H^3O,C^8H^7O^3$ = Valerianic acid, $C^{10}H^{11}O^4$.

Butyrate of ethyl, $C^4H^5O,C^8H^7O^3$ = Formiate of amyl, $C^{10}H^{11}O,C^2HO^3$, and Valerate of methyl, $C^2H^3O,C^{10}H^9O^3$ = Caproic acid, $C^{12}H^{12}O^4$.

Caproate of methyl, $C^2H^3O,C^{12}H^{11}O^3$, and Valerate of ethyl, $C^4H^5O,C^{10}H^9O^3$ = Oenanthylic acid, $C^{14}H^{14}O^4$.

Oenanthylate of methyl, $C^2H^3O,C^{14}H^{13}O^3$, and Caproate of ethyl, $C^4H^5O,C^{12}H^{11}O^3$ = Caprylic acid, $C^{16}H^{16}O^4$.

Valerate of amyl, $C^{10}H^{11}O,C^{10}H^9O^3$ = Capric acid, $C^{20}H^{20}O^4$, and = 2 Valeral = $2C^{10}H^{10}O^2$.

Salicylate of methyl, $C^2H^3O,C^{14}H^5O^5$ = Anisic acid, $C^{16}H^8O^6$.

Metameric compounds like those just adduced, may have the same specific gravity in the gaseous state; but in the liquid state, they differ both in density and in boiling point, the density and boiling point of compound ethers being lower than those of the acids with which they correspond in number of atoms.

3. The following is a perfectly unique case of metamerism or isomerism, produced by nitrogen entering into one compound as an element, into another as amidogen, and into a third as hyponitric acid; $C^{14}H^7NO^4$ is the empirical formula of Anthranilic acid, Benzamic acid, Salicylamide, and Nitrotoluidine; but the rational formula of Anthranilic acid is $C^{14}H^7NO^4$; of Benzamic acid, $C^{14}H^5AdO^4$; of Salicylamide, $C^{14}H^5AdO^2,O^2$; and of Nitrotoluidine, $C^{14}H^7X$.

IV. Decompositions and Transformations of Organic Compounds.

We may safely assume that the chemical force which unites the elements of an organic compound is in most cases weaker than that by which inorganic compounds, such as carbonic oxide, carbonic acid, water, sulphide of carbon, sulphuretted hydrogen, phosphuretted hydrogen, and ammonia, are held together, and that the constituents of the more simple organic compounds, such as marsh-gas (C^2H^2), olefiant-gas (C^4H^4), cyanogen (C^2N), &c., are united by a stronger affinity than those of the more complex substances. These affinities, which tend to restore the constituents of an organic compound to the inorganic state, together with the great affinity of heat for hydrogen and nitrogen, which favours their evolution in the gaseous form, might be expected to produce a speedy decomposition of organic compounds, after the death of the plant or animal which has produced and maintained them during its life. Nevertheless, under certain external circumstances, especially at low temperatures and out of contact of air, they remain unaltered even after the death of the plant or animal. The elementary atoms, by a peculiar *vis inertiæ*, remain in the relative position into which they were brought when the organic compound was formed, although the affinities which tend to the formation of gases and the production of carbonic acid, water, &c., are in reality of greater intensity. Slight causes, however, are sufficient to bring these stronger affinities into action, and then the original organic compound is decomposed, with evolution of hydrogen and nitrogen gases, and formation of the above-mentioned inorganic compounds, or of organic compounds of lower order and held together by stronger affinities. The same phenomenon is likewise exhibited by inorganic compounds: Nitrite of ammonia is resolved at 50° into water and nitrogen gas, and nitrate of ammonia, at 238°, into water and nitrous oxide.

The transformations of organic compounds may take place in the following ways:

1. Conversion of one isomeric, polymeric, or metameric compound into another (pp. 66—69).

2. Substitution.

3. Absorption of one or more substances into the organic compound from without:—Absorption of *oxygen:* Aldehyde, $C^4H^4O^2$, is converted into acetic acid, $C^4H^4O^4$;—of *hydrogen:* Indigo-blue, $C^{16}H^5NO^2$, into indigo-white, $C^{16}H^6NO^2$; chinone, $C^{12}H^4O^4$, into green and colourless hydrochinone, $C^{12}H^6O^4$ and $C^{12}H^8O^4$; of *hydrogen and oxygen* together: Isatine, $C^{16}H^5NO^4$, is converted, by the action of aqueous potash, into isatinic acid, $C^{16}H^7NO^6$; oil of turpentine, $C^{20}H^{16}$, by taking up 4HO, is converted into turpentine-camphor, $C^{20}H^{20}O^4$.

4. Complete or partial abstraction of one or more constituents (carbon excepted). Alcohol is converted into aldehyde by abstraction of 2H, into ether by abstraction of HO, and into olefiant gas, by removal of 2HO. Malic acid is resolved by heat into water and maleic acid.

5. Resolution into several new organic, or partly also inorganic compounds: separation, *dédoublement.*—Chloral, $C^4HCl^3O^2$, treated with aqueous potash, is resolved, with decomposition of 2HO, into formic acid, $C^2H^2O^4$, and chloroform, C^2HCl^3; acetic acid, $C^4H^4O^4$, ignited with excess of baryta, is resolved into marsh-gas and 2 At. carbonic acid, C^2O^4.

6. Complete decomposition into inorganic compounds and elements:—By the complete combustion of organic compounds;—by passing some of them through red-hot porcelain tubes;—by treating oxalic acid with oil of vitriol.

1. *Substitution or Metalepsy.*

This term, taken in its widest sense, may include all decompositions, in which, by the action of a simple substance, or of an inorganic or even an organic compound, any element of an organic substance, excepting carbon, is wholly or partially withdrawn, and its place in the organic compound is supplied by an equal number of atoms of another simple substance or of another compound, organic or inorganic,—so that we may suppose that the atoms of the new substance, simple or compound, take the places previously occupied by the substance which has been removed, and therefore, not only the number of atoms in the compound, but likewise their relative position, remains the same.

The carbon of an organic compound cannot be removed by substitution; for this element is the one essential principle of organic compounds; the number of its atoms determines their character; and no other substance can take its place. Without carbon, nothing organic can exist! Even the diminution of the number of its atoms in a compound would immediately remove that compound into another series, and alter its character entirely.—Walter's supposition that in sulphocamphoric acid, 2C are replaced by 2SO, is utterly inadmissible. It is only when the substitution-theory admits the possibility of replacing carbon-atoms by others, that it deserves the ridicule sometimes cast upon it. (*Ann. Pharm.* 33, 309.)

The removal of one of the elements of an organic compound by the action of any substance, is not always followed by a true substitution.

Sometimes certain constituents of a compound are removed without any substitution:—Thus, alcohol, $C^4H^6O^2$, is deprived by the oxygen of nitric acid, &c., of 2 At. H, and there remains aldehyde, $C^4H^4O^2$.—Similarly, 1O of the air takes away 1H from indigo-white, $C^{16}H^6NO^2$, forming water, and leaves indigo-blue, $C^{16}H^5NO^2$.

In other cases, the replacement of the original substance by the new one is incomplete.—Thus, by the continued action of chlorine upon alcohol, 5H are removed, but only 3Cl enter into the new compound, chloral:

$$C^4H^6O^2 + 8Cl = C^4HCl^3O^2 + 5HCl.$$

In other cases, again, the compound, after substitution, contains more atoms than before,—sometimes because the compound formed by the

substitution of the corresponding number of atoms of the introduced substance, takes up an additional number of them (outside the nucleus); sometimes, again, because it retains the compound formed by the union of the abstracted substance with the decomposing body, in a state of loose combination (likewise outside the nucleus).—An instance of the former case is afforded by olefiant-gas, C^4H^4, which, when treated with chlorine in sunshine, is ultimately converted into C^4Cl^6:

$$C^4H^4 + 10Cl = C^4Cl^6 + 4HCl.$$

In this case, the true substitution-product of C^4H^4, namely, C^4Cl^4, takes up two additional atoms of chlorine.—An example in which the decomposition-product formed in the substitution—that is to say, the compound formed by the union of the abstracted element and the acting substance—remains combined with the organic compound altered by substitution, is afforded by benzole, $C^{12}H^6$. This substance, when treated with excess of chlorine, yields $C^{12}H^6Cl^6$, or more properly, $C^{12}H^3Cl^3$, 3HCl; and when the 3HCl are removed by potash, the true substitution-product $= C^{12}H^3Cl^3$, remains.

In many organic compounds, it is possible to effect the complete removal of one of the constituents, hydrogen, for example, by substitution, if the substance which produces the substitution be allowed to act in sufficient quantity and under fitting circumstances (of heat, light, &c.). In such a case, as one after another of the removable substances is replaced, the original compound passes through several definite intermediate stages to the last stage, in which one of the elements of the original compound has completely disappeared. Thus, hydrochloric ether, C^4H^5Cl, when exposed to the action of chlorine, at continually higher degrees of light and heat, is converted, first into $C^4H^4Cl^2$, then into $C^4H^3Cl^3$, then into $C^4H^2Cl^4$, then into C^4HCl^5, and finally into C^4Cl^6.

In other compounds, only a portion of the hydrogen-atoms can be removed by substitution, as in $C^{12}H^6$, $C^{20}H^{16}$, &c.

Substitution may take place in the following ways:

1. One or more atoms of the substance which acts on the organic compound, unite with one or more atoms of the removable element, and form an inorganic compound, while other atoms of the acting body, equal in number to the abstracted atoms of the removable substance, enter the organic compound:—Thus, for example, in the substitution of hydrogen by chlorine:

$$\underbrace{C^4H^4O^4}_{\text{Acetic acid.}} + 6Cl = 3HCl + \underbrace{C^4HCl^3O^4}_{\text{Chloracetic acid.}}.$$

2. A compound body acts upon the organic substance, one of its constituents uniting with the removable substance, while another portion takes the place of the latter in the organic compound.—Thus, in the substitution of hyponitric acid for hydrogen by the action of nitric acid, or of sulphurous acid for hydrogen, by the action of sulphuric acid, or of NH for 2O by the action of ammonia:

$$C^{12}H^6 + NO^5 = HO + C^{12}H^5NO^4 (= C^{12}H^5X).$$
$$C^{12}H^6 + SO^3 = HO + C^{12}H^5SO^2.$$
$$C^{12}H^6,O^2 + NH^3 = 2HO + C^{12}H^7N.$$

a. Hydrogen is the element most frequently replaced, and by the following substances:

By *Chlorine, Bromine,* and *Iodine.*—Aldehyde is converted by chlorine into hydrochloric acid and chloral:

$$C^4H^4O^2 + 6Cl = 3HCl + C^4HCl^3O^2.$$

Benzole acted upon by bromine is first converted into hydrobromate of bromobenzide:

$$C^{12}H^6 + 6Br = C^{12}H^3Br^3,3HBr;$$

but when the 3HBr are removed by caustic potash, bromobenzide = $C^{12}H^3Br^3$ alone remains.—Olefiant gas, C^4H^4, yields, with iodine, first, C^4H^3I, HI, and after withdrawal of the HI by potash, C^4H^3I.—Hydrocyanic acid, C^2NH, with 2Cl, yields HCl and chloride of cyanogen, C^2NCl.

Compounds in which hydrogen is replaced by chlorine, bromine, or iodine, possess the character of the original compounds. Thus, not only do acid compounds retain their acid character, and neutral compounds their neutral character, but even basic compounds retain their basic character, in a less degree, however, as the number of hydrogen-atoms removed is greater; *e. g.*, in Aniline. The compounds in which hydrogen is replaced by chlorine or bromine likewise exhibit with sulphurous acid, hydrosulphate of ammonia, heated potash, &c., reactions exactly corresponding to those which are exhibited under similar circumstances by the original compounds. The chlorine, bromine, or iodine in these compounds is not indicated by solution of silver, not even when the compounds insoluble in water are dissolved in alcohol; the reaction does not take place till they are decomposed.

By *Oxygen.*—Alcohol by taking up oxygen and parting with hydrogen, is converted into acetic acid:

$$C^4H^6O^2 + 4O = 2HO + C^4H^4O^4.$$

(Gerhardt does not admit the substitution of H by O, S, Se and Te, which in fact would not agree with the double atomic weights [in comparison with that of H], which he assigns to those elements (p. 28); he supposes, therefore, that in the conversion of alcohol into acetic acid, only 1 At. O enters the compound for every 2 At. H withdrawn, so that the resulting compound contains a smaller number of atoms: $C^2H^6O + 2O = H^2O + C^2H^4O^2$.)

By *a Metal.* Many metallic salts of organic acids in their greatest state of dryness, may be regarded as acids dried *per se*, in which, according to the monobasic or polybasic character of the acid, one or more atoms of hydrogen are replaced by an equal number of atoms of a metal; *e. g.*,

$$C^4H^4O^4 + KO = HO + C^4H^3KO^4.$$

By *Hyponitric acid.* When strong nitric acid acts upon an organic compound containing hydrogen, its fifth atom of oxygen often combines with hydrogen, forming the compound HO, and $NO^4 = X$ takes the place of the hydrogen.—Thus, when Benzole is dissolved in strong nitric acid and water added, Nitrobenzide separates out:

$$C^{12}H^6 + NO^5 = HO + C^{12}H^5NO^4 \ (= C^{12}H^5X).$$

Similarly, Benzoic acid, $C^{14}H^6O^4$, is converted by strong nitric acid into Nitrobenzoic acid, $C^{14}H^5XO^4$; Salicylic acid, $C^{14}H^6O^6$, into Indigotic

acid, $C^{14}H^5XO^6$; and Cinnamic acid, $C^{18}H^8O^4$, into Nitrocinnamic acid, $C^{18}H^7XO^4$.

It would appear that not more than 3 At. H of a compound can be replaced by NO^4; if too much hyponitric acid accumulates in the compound, its oxygen burns the carbon, and complete decomposition takes place. Compounds retain their original chemical character, even after the substitution of NO^4 for H. Hence the new compound exhibits acid characters, only when the original compound was an acid. The acid character, however, is strengthened by the substitution. The resulting compounds are generally yellow; most of them deflagrate when heated—if they do not evaporate unaltered—because, like gunpowder, they contain carbon together with the loosely combined oxygen of the hyponitric acid; they detonate with sodium under the hammer. They give off red fumes, when heated with oxide of manganese and sulphuric acid, or when heated alone, or in presence of chlorine gas, even without contact of air.

These nitro-compounds might be regarded as combinations of nitrous acid with an organic oxide, corresponding to the compound ethers. Viewed in this light, Nitrobenzide would not be $C^{14}H^5NO^4$, but $C^{14}H^5O,NO^3$; in that case, however, Binitrobenzide, $C^{14}H^4N^2O^8$, must, to be consistent, be expressed by the formula $C^{14}H^5O^2,2NO^3$, which contains 1 At. H more than is given by analysis. A still stronger objection is found in the fact, that these compounds are not converted by potash into nitrous acid and the oxide supposed to exist in them, as their assumed analogy with the compound ethers might lead us to expect.

By *Sulphurous acid.* When strong sulphuric acid acts upon organic compounds, its third atom of oxygen sometimes forms water with part of the hydrogen in the compound, and SO^2 takes the place of the hydrogen.—Anhydrous sulphuric acid with benzole forms sulphobenzide and water:

$$C^{12}H^6 + SO^3 = C^{12}H^5(SO^2) + HO.$$

Mitscherlich (*Pogg.* 31, 631) first showed, in 1834, that nitric and sulphuric acid can enter so intimately into an organic compound in the forms of NO^4 and SO^2—with separation of water—as to lose their acid character.

¶ By *Organic Radicals,* such as *Methyl, Ethyl, Amyl, Phenyl,* &c. This substitution is seen in the new compound ammonias discovered by Wurtz and Hofmann, in which one or more of the hydrogen-atoms in ammonia is replaced by methyl, ethyl, &c.; *e. g.,* Methylamine = $NH^2(C^2H^3)$; Ethylamine = $NH^2(C^2H^5)$; Diamylamine = $NH(C^{10}H^{11})^2$; Triethylamine = $N(C^4H^5)^3$; Diethylamylamine = $NH(C^4H^5)(C^{10}H^{11})$, &c., &c. (p. 17.) ¶

b. Chlorine, Bromine, and *Iodine* are replaced:

By *Hydrogen.* This substitution is effected by means of potassium, zinc, &c.; also at the negative pole of the electric circuit, in presence of water.—Acetic acid, $C^4H^4O^4$, may be converted by chlorine into chloracetic acid, $C^4HCl^3O^4$, and the latter may be reconverted into acetic acid in the form of a potash-salt, by bringing it, in the dilute state, into contact with potassium-amalgam. (Melsens.) 3K take up 3Cl; 1K goes over to the acetic acid, and 2K transfer 2H from the water to the acid:

$$C^4HCl^3O^4 + 6K + 2HO = C^4KH^3O^4 + 3KCl + 2KO.$$

By *Amidogen.* Ammonia acting upon compounds containing Cl, Br,

or I, gives up its third atom of hydrogen to the chlorine, bromine, or iodine, and NH^2 passes into the compound, while HCl, HBr, or HI is separated, and combines with the excess of ammonia.—Chlorobenzoyl with ammonia yields benzamide and hydrochloric acid:

$$C^{14}H^5ClO^2 + NH^3 = C^{14}H^5(NH^2)O^2 + HCl.$$

By *Sulphur*. Sulphide of potassium acts on certain organic compounds in such a manner as to form chloride of potassium, while sulphur enters the compound in place of the chlorine.—The compound of olefiant gas with chlorine=$C^4H^4Cl^2$ forms with 2 At. KS dissolved in alcohol: 2KCl and $C^4H^4S^2$. Similarly, hydrochloric ether, C^4H^5Cl, with KS dissolved in alcohol, yields KCl and C^4H^5S (sulphide of ethyl); and with KS,HS, dissolved in alcohol, it yields KCl and $C^4H^6S^2$ (mercaptan).

c. Hyponitric acid may be replaced:

By *Amidogen*, when the compound containing NO^4 is acted upon by hydrosulphuric acid, either free or combined with ammonia. In this case, the N of the NO^4 remains in the compound, but gives up its 4O to 4H of the hydrosulphuric acid, taking in its place 2H from 2 other atoms of HS, to form amidogen. Hence, for each atom of NO^4 converted into amidogen, 6HS are decomposed and 6S precipitated.—This change is exemplified by the conversion of Nitrobenzoic acid into Benzamic acid:

$$C^{14}H^5(NO^4)O^4 + 6HS = C^{14}H^5(NH^2)O^4 + 4HO + 6S;$$

also by the conversion of Nitrobenzide into Aniline:

$$C^{12}H^5NO^4 + 6HS \quad C^{12}H^7N + 4HO + 6S;$$

of Nitronaphthaline, $C^{20}H^7NO^4$, into Naphthalidam, $C^{20}H^9N$; and of Binitrobenzide into Nitraniline:

$$C^{12}H^42(NO^4) + 6HS = C^{12}H^4(NO^4)(NH^2) + 4HO + 6S.$$

Hyponitric acid may also be replaced by *Nitrogen*.—Thus Nitrobenzide, $C^{12}H^5X$, when heated with alcoholic potash, is converted into Azobenzide, $C^{12}H^5N$, with formation of oxidation-products of the alcohol by the 4O of the NO^4.

d. Oxygen in an organic compound may be replaced:

By *Amidogen*, by the action of ammonia. The latter compound is frequently resolved by the oxygen of the organic substance into HO and NH^2, which enters in place of the oxygen.—At the same time, 1 At. HO escapes from the compound. Salicylate of ammonia, when heated, is resolved into water and Salicylamide:

$$NH^3,C^{14}H^6O^6 = 2HO + C^{14}H^5NH^2O^4 \ (= C^{14}H^5AdO^4).$$

By *Nitrogen*, likewise from the action of ammonia; inasmuch as, in certain cases, all the 3H of the ammonia appear to combine with 3O from the organic compound and form water, so that the 3O are replaced by 1N. This case then does not strictly come under the head of substitutions, because the numbers of atoms of the substituting and substituted body are unequal; and the new compound does not belong to the same type as the original.—Thus 3 At. Bitter almond oil with 2 At. ammonia, form 6 At. water and Hydrobenzamide, or some other compound isomeric with the latter:

$$3C^{14}H^6O^2 + 2NH^3 = 6HO + C^{42}H^{18}N^2.$$

Here then 6O are replaced by 2N; moreover, 3 At. of one compound are required to form 1 At. of the other, which is held together by 2N.

Laurent likewise supposes that, in certain cases, 1O is replaced by 1 At. *Imidogen* = Im. This he regards as composed of $\frac{1}{2}$ At. N + $\frac{1}{2}$ At. H, or 1 At. N + 1 At. H, taking the atomic weights as given by Berzelius. But the cases in which 1 At. Imidogen must be supposed to exist in a substituted compound are doubtful; and in those compounds, which Laurent supposes to contain 2Im, we may just as well write NH. But N^2H^2 might in some few cases be written as Im^2.

By *Sulphur*, acting in the form of hydrosulphuric acid or a metallic sulphide.—Alcohol, as it exists in sulphovinate of baryta, is converted by sulphide of hydrogen and barium into mercaptan, $C^4H^6S^2$:

$$(BaO,SO^3 + C^4H^6O^2,SO^3) + BaS,HS = 2(BaO,SO^3) + HO + C^4H^6S^2.$$

Bitter almond oil acted upon by sulphuretted hydrogen in combination with ammonia, forms sulphobenzene and water:

$$C^{14}H^6O^2 + 2HS = C^{14}H^6S^2 + 2HO.$$

By *Tellurium*. In the formation of telluride of ethyl from sulphovinate of baryta and telluride of sodium.

e. Sulphur may be replaced:

By *Oxygen;* as by the action of metallic oxides, which form metallic sulphides, and transfer their oxygen to the organic compound.—Oxide of silver, under certain circumstances, decomposes oil of garlic, C^6H^6S, forming oxide of allyl, C^6H^6O, and sulphide of silver.

For the replacement of any substance by *Arsenic* or by *Arside* = AsH^2, *vid. Cacodyl.*

Gerhardt's Law of Residues.

Whenever one atom of an element in an organic compound is replaced by one atom of another compound, organic or inorganic, a certain quantity of water separates out, formed, according to nature of the compounds, sometimes from the hydrogen of the first compound and the oxygen of the second, sometimes from the hydrogen of the second and the oxygen of the first. The compound thus formed by substitution contains therefore the residues of the two compounds united, that is to say, the first compound + the second, *minus* an equal number of H- and O-atoms.

Accordingly, Gerhardt assumes the existence of the following residues:

Ammonia	$NH^3 - H^2 = NH$	= Am	(different, therefore, from Laurent's Am = NH^2)	
Arseniuretted Hydrogen	$AsH^3 - H^2 = AsH$	= Ar	(different, therefore, from Laurent's Ar = Arside = AsH^2)	
Hydrate of Nitric acid	$NHO^6 - O^2 = NHO^4$	= Ni		
Oil of Vitriol	$S^2H^2O^8 - O^2 = S^2H^2O^6$	= Su		
Hydrate of Phosphoric acid	$PH^3O^8 - O^2 = PH^3O^6$	= Ph		
Formic acid	$C^2H^2O^4 - O^2 = C^2H^2O^2$	= Fo		
Acetic acid	$C^4H^4O^4 - O^2 = C^4H^4O^2$	= Ac		
Wood-spirit	$C^2H^4O^2 - H^2 = C^2H^2O^2$	= Me		
Alcohol	$C^4H^6O^2 - H^2 = C^4H^4O^2$	= E	(therefore = Ac)	
Aniline	$C^{12}H^7N - H^2 = C^{12}H^5N$	= An		

Examples: Oxalic acid, $C^4H^2O^8$, with $2NH^3$, yields 4HO, and Oxamide, $C^4H^4N^2O^4$. This may be regarded as a compound of the two residues, $C^4H^2O^4$ and 2NH.

Benzine, $C^{12}H^6$, with concentrated nitric acid, HO,NO^5, yields 2HO and Nitrobenzide$=C^{12}H^5NO^4$ $(=C^{12}H^5X)$; according to Gerhardt's view $=C^{12}H^4(NHO^4)$.

1 At. Wood-spirit, $C^2H^4O^2$, with 2 At. sulphuric acid, forms Sulphomethylic acid$=C^2H^4O^2,2SO^3$. This reaction is expressed by Gerhardt as follows:

$$C^2H^4O^2 + S^2H^2O^8 - 2HO = C^2H^2O^2 + S^2H^2O^6 = Me + Su.$$

[But the residue of sulphuric acid cannot always be expressed by $S^2H^2O^6$. Thus, Wood-spirit, $C^2H^4O^2$, and SO^3 form HO and sulphate of methyl$=C^2H^3O,SO^3$. In this case, Gerhardt doubles the formulæ, because he estimates the atomic weights of S and O at twice their usual values, and therefore supposes 2 At. of oil of vitriol, as given in this Hand-book $=S^2H^2O^8$, (or according to his own atomic weights, SH^2O^4,) to be concerned in the action. Thus, 2 At. wood-spirit, $C^4H^8O^4$, with $S^2H^2O^8$, form 4HO and 2 . $C^2H^2O^2+S^2H^2O^4$; and since the sulphuric acid must have given up 4O to form 4HO, its residue must be $S^2H^2O^4$.]

Alcohol, $C^4H^6O^2$, with formic acid, $C^2H^2O^4$, yields 2HO and formic ether$=C^6H^6O^4$. This, according to the ordinary view, $=C^4H^5O+C^2HO^3$; according to Gerhardt's, it is $C^4H^4O^2+C^2H^2O^3=E+Fo$; &c.

2. *Decompositions by Heat.*

a. Dry or *Destructive Distillation.*—Some organic compounds boil at so low a temperature that, when heated in a retort, they pass over unchanged, especially if the air be excluded; *e. g.*, Alcohol, ether, volatile oils.—The air in the apparatus may form more fixed products by oxidation, and these will not pass over without decomposition; *e. g.*, small quantities of resin formed from volatile oils.

Other organic compounds, on the contrary, which would not boil till raised to a higher degree of heat, undergo, before they attain the boiling temperature, that kind of decomposition called, *Decomposition by Dry or Destructive Distillation.*

Compounds whose boiling points are not much above the temperatures at which their decomposition begins, pass over to a certain extent undecomposed. For the vapours and gases produced by the decomposition of the one part, take up the other part of the compound below the boiling temperature in the form of vapour, just as water evaporates in the air considerably below its boiling point (I., 266).—Thus, oxalic acid, margaric acid, and other fatty acids, also pinic acid, and certain other resins, indigo-blue, &c., undergo but partial decomposition. Such compounds may therefore be volatilized without decomposition, if they be heated in open vessels to a temperature somewhat below that at which they decompose; or in a wide distillatory apparatus filled with air; or in a tube or a conical enlargement of it, through which is passed a stream of air—or if the air exerts an oxidizing action—of hydrogen, nitrogen, or carbonic acid gas; also when carefully heated in vacuo. (*Comp.* Gay-Lussac, *Ann. Chim.* 74, 189; also *N. Gehl.* 9, 765.)

A contrary action is exerted by sand, brickdust, &c., mixed in large quantities with the organic compound, even if the boiling point of that compound be below the temperature at which it decomposes; for the

bubbles of vapour are mechanically retained by the pulverulent mixture, and raised by the heat which penetrates the containing vessel, to the degree at which their decomposition takes place. Alcohol is partially decomposed by this treatment, and benzoic acid almost completely.

The causes of decomposition by heat are as follows: The affinity of the oxygen for the hydrogen and the carbon tending to form water, carbonic oxide and carbonic acid, is greater than that by which the elements in the organic compound are held together. These strong affinities are brought into action by heat. Hence those compounds which contain most oxygen decompose at much lower temperatures than those which contain little or none.—To this rule, however, there are many exceptions: Acetic acid, $C^4H^4O^4$, is a body rich in oxygen; but its vapour is but little altered in composition by passing through a tube at a low red heat; acetate and cyanate of potash also, are not decomposed when heated to low redness out of contact with air.

In compounds containing nitrogen, the affinity of that element for hydrogen likewise assists the decomposition. The ammonia which is then abundantly formed, does not, however, pass over in the free state, but in combination with an acid, as with carbonic, acetic acid, &c.

If the compound contains chlorine, bromine, iodine, or sulphur, these elements, if they do not separate in the free state, or enter into volatile organic compounds, are given off in combination with hydrogen, in the form of hydrochloric, hydrobromic, hydriodic, or hydrosulphuric acid. Part of the sulphur and chlorine may also be evolved in the form of sulphide or chloride of carbon.

At high temperatures, moreover, decomposition is facilitated by the affinity of heat for those elements which have a great tendency to assume the gaseous form: hence part of the hydrogen and nitrogen are given off in the state of gas, the quantity thus evolved increasing with the temperature; for even the hydrocarbons formed at a moderate heat may be resolved at higher temperatures into hydrogen gas and sooty carbon. The heat may also induce a disposition for the formation of volatile organic compounds, which, when once produced, pass over, and are thus withdrawn from the decomposing action of a stronger heat.

By the formation of the inorganic compounds above mentioned, and by the escape of hydrogen and nitrogen gas, the organic compound (unless it be one of the more highly oxygenized acids, such as oxalic or formic acid) loses oxygen in the greatest *relative* quantity, hydrogen and nitrogen in smaller quantity, while the residue becomes continually richer in carbon.

Hence those volatile organic compounds which are richest in oxygen, such as acids and alcoholic liquids, pass over principally at the beginning of the distillation. Among *Acids*, the most frequent is acetic acid. It is formed in especial abundance in the distillation of compounds, such as sugar, gum, or wood, which contain oxygen and hydrogen in about equal numbers of atoms, so that it only requires the addition of an equal number of carbon-atoms to form acetic acid, $C^4H^4O^4$, which, being volatile, is withdrawn from the further decomposing action of the heat. Many organic compounds yield other acids, which in some cases are quite peculiar to them (*vid. inf.*). The alcoholic liquids produced in the dry distillation of a few organic compounds are, Wood-spirit, Lignone, Aldehyde, and Acetone.

But as the distillation proceeds, compounds containing little or no

oxygen appear in continually greater abundance, viz.: 1. *Gaseous Hydrocarbons*, such as marsh-gas, C^2H^4, olefiant gas, C^4H^4, the gas of Faraday's most volatile empyreumatic oil, C^8H^8. The last two hydrocarbons are evolved chiefly from compounds containing but little oxygen, such as fats and resins; the greater their proportion in the gaseous mixture, the more brilliant is its flame and the better is it adapted for illumination.—2. Volatile oils generally having an offensive odour, and designated, from their mode of formation, as *Empyreumatic Oils*. They are hydrocarbons, sometimes pure, sometimes slightly oxidized. To this class of products belong the two empyreumatic oils which Faraday obtained from fat, also eupione, creosote, picamar, and kapnomor, obtained by Reichenbach, pyrrol by Runge, and several oils obtained from resins by Frémy, Couerbe, Laurent and others; &c. &c.—3. *Camphoroidal compounds*, which may be called *Empyreumatic Camphors* or *Stearoptenes* in general; they consist wholly of carbon and hydrogen; but some of them appear to be produced from other volatilized compounds, which are subjected to the further action of a red heat within the apparatus.—4. Resins, which may be called *Empyreumatic Resins*, containing but little oxygen, and generally dark-coloured; according to Unverdorben, some of them dissolve both in alcohol and in potash, others only in alcohol, others again only in potash.—5. If the original compound contains nitrogen, *Volatile Alkaloids* are also given off, such as Aniline, $C^{12}H^7N$, Leukol, $C^{18}H^7N$, Odorine, Animine, Olanine and Ammoline, according to Unverdorben.—¶ Anderson has obtained, from the distillation of bone-oil, three series of bases, viz., (1.) ammonia and a series of bases homologous with it, viz., Methylamine, C^2H^5N, Ethylamine, C^4H^7N, Propylamine, C^6H^9N, Butylamine (petinine), $C^8H^{11}N$, Amylamine, $C^{10}H^{13}N$, and probably also Caproamine, $C^{12}H^{15}N$; these bases all volatilize below 240°.—(2.) A series of bases boiling above 240°, peculiar to the oil, homologous with one another, and remarkable for their isomerism with the series of which aniline is the type; these are: Pyridine, $C^{10}H^5N$; Picoline, $C^{12}H^7N$, isomeric with aniline; and Lutidine, $C^{14}H^9N$, isomeric with toluidine.—(3.) A series of bases homologous with Runge's pyrrol, and therefore designated provisionally as *Pyrrol-bases;* they appear to be coupled substances, consisting of members of the picoline-series in combination with a red matter, which separates when they are heated with an excess of hydrochloric acid. (Anderson, *Ed. Phil. Trans.* 20, 2, 247; abstr. *Chem. Soc. Qu. J.* 5, 50.) ¶

As the more volatile products escape, substances of continually diminishing volatility remain behind; and these, as the temperature rises, are either evolved unaltered in the gaseous form, or resolved into more volatile matters and residual products of still greater fixity.

The hydrogen, nitrogen, and oxygen, which finally remain, are either sufficient to form, with the whole of the residual carbon, a compound which is volatile at a higher temperature, in which case nothing remains in the retort; or, the relative quantity of the carbon is too great to enter wholly into such a state of combination; and then, as the heat approaches to redness, this excess remains behind in the form of charcoal, still combined with small quantities of the other substances, which, however, are separated the more completely as the residue is finally subjected to a stronger heat.

Compounds containing a medium quantity of oxygen, such as sugar, gum, wood, and glue, leave, if they are not volatile, the largest quantity of charcoal; because a large portion of the hydrogen, which would other-

wise volatilize the carbon, is converted by the oxygen into water. These compounds leave more charcoal in proportion as they are heated more slowly, because the quantity of water formed is then likewise greater.—When the proportion of oxygen is large, this element also tends to volatilize the carbon, in the form of carbonic acid and carbonic oxide.—When the quantity of oxygen is comparatively small, the hydrogen combines chiefly with the carbon, forming volatile compounds, such as gases, oils, camphors, and resins.

If the compound, during dry distillation, passes into a fused or softened state, which is most frequently the case, the charcoal appears inflated, like that formed from resin and sugar, or at all events very porous, like that from tartaric acid and cork. But if the compound, wood, for example, remains solid while subjected to heat, the charcoal still exhibits the original form and internal structure, but is contracted in volume.

So long as the original compound is uniformly exposed to a comparatively gentle heat, the products formed are different from those which make their appearance at a higher temperature; the residue which remains after the more gentle heating, and resists decomposition at this temperature, suffers a further decomposition at a certain higher temperature, yielding new volatile products, and leaving a still more fixed residue, which is not decomposed till raised to a yet higher temperature, when it again yields new products, &c. &c., till finally nothing but charcoal remains.

Spongy platinum, inasmuch as it favours the formation of vapour in liquids (II., 275, 3), may cause an organic compound to be completely resolved into volatile products at a lower temperature than it would if heated alone. Thus, tartaric acid mixed with spongy platinum and carefully heated, yields nothing but carbonic acid and a transparent and colourless, crystallizable distillate. (Reiset & Millon.)

The products of dry distillation may be arranged in the following classes, according to their external forms:

1. *Gases:* Hydrogen and nitrogen;—carbonic oxide, carbonic acid, hydrochloric, hydrobromic, hydriodic, and hydrosulphuric acid gases;—marsh-gas, olefiant gas, and the gas from Faraday's most volatile empyreumatic oil, C^8H^8. In this gaseous mixture, the vapours of empyreumatic oils and of sulphide of carbon are also diffused.

2. *Watery Distillate.* The water contained in this distillate was either attached as such to the organic compound, or it has been formed at the high temperature to which that compound has been subjected, from the oxygen and hydrogen contained in it. In this water are dissolved: *a.* In some few instances, alcoholic fluids, such as aldehyde, wood-spirit, lignone, and acetone.—*b.* Almost always acids, of which the most frequent is acetic acid. Hence the watery distillate obtained in the dry distillation of non-azotized organic bodies almost always has an acid reaction. — *c.* The watery distillate obtained from azotized substances contains small quantities of hydrocyanic acid and large quantities of ammonia. When the quantity of that base is but small, it is completely saturated by the acetic acid or any other stronger acid that may be present, and the watery distillate still exhibits an acid reaction, or is neutral; but in the distillate obtained from most azotized bodies, these stronger acids are not present in sufficient quantity to neutralize the large quantity of ammonia, the excess of which, therefore, unites with

the carbonic acid, and in the form of carbonate of ammonia, imparts an alkaline reaction to the liquid. By this character, a non-azotized organic compound may be distinguished from one which contains nitrogen. The former yields an acid distillate, which does not give off ammonia even on the addition of potash; the latter gives either an alkaline distillate, or, if it contains but little nitrogen, a neutral or acid distillate, which gives off ammonia when treated with potash. But a non-azotized organic compound likewise yields ammonia by destructive distillation, if it be previously mixed with nitre. Thus, gum-arabic distilled with one-tenth of its weight of nitre yields ammonia and a pyrophoric charcoal containing cyanide of potassium. (Vauquelin, *Ann. Chim.*. 72, 59).—¶ The watery distillate from azotized organic substances may also contain volatile organic alkaloids. (Anderson.) ¶—*d.* The watery distillate likewise holds in solution a small quantity of the tarry matter next to be considered, which gives it a brown colour.

3. *Oily* or *Tarry Distillate, Empyreumatic Tar.*—Generally a brown and fetid mixture of different empyreumatic oils, camphors and resins, which, according to Unverdorben, may likewise contain volatile alkaloids, a brown mouldy substance, and another brown substance soluble in water and alcohol, and forming with potash baryta and lime, compounds which are soluble in water, and, with the earths, compounds which are insoluble. [The oily bases discovered by Anderson in the *Oleum animale Dippelii* have already been mentioned (p. 79)]. The most fetid tar is that obtained from the more highly azotized compounds, such as gelatine and white of egg. The offensive odour of most empyreumatic tars is ascribed by Unverdorben (*Pogg.* 8, 253, 297, and 477) to a peculiar oily acid which he calls *empyreumatic acid* (*Brandsäure*), but which varies with the nature of the original compound, being sometimes lighter, sometimes heavier, than water.

4. *Sublimed Products.*—These products consist sometimes of an acid, *e. g.*, pyrogallic acid, sometimes of a camphor, sometimes of carbonate of ammonia.

5. Charcoal.

Some organic compounds yield all these products, viz., gases, watery liquid, tar, sublimate, and charcoal. Such is the case with gelatin, albumen, &c., in which the sublimate consists of carbonate of ammonia.—Other compounds, as sugar, woody fibre, &c., yield gases, a watery liquid, tar, and charcoal, but no sublimate.

Many acids are wholly resolved into water or carbonic acid (or both together), and one or more acids, called *Pyro-acids*, containing less oxygen. The decomposition is not attended with evolution of gas,—excepting in some cases, carbonic acid,—or with separation of charcoal, especially if the heat be carefully applied, so that the new compounds, at the moment of their evolution, may not be exposed to a stronger heat, and thereby resolved into charcoal and more complicated products. Distillation of this kind is distinguished by Pelouze (*Ann. Chim. Phys.* 56, 303), who has described several instances of it, by the term *White Distillation* (*Distillation blanche*), the other form of the process, in which charcoal remains behind, being called *Black distillation* (*Distillation noire*).

Malic acid (considered as bibasic), when quickly heated to 200°, is almost completely resolved into water and maleic acid, which distil over:

$$C^8H^6O^{10} = 2(C^4H^2O^4) + 2HO.$$

At 150°, it yields, as principal product, a residue of fumaric acid, which

is polymeric with maleic acid, and may be regarded as a bibasic acid $=C^8H^4O^8$. At a more intense heat, the products are carbonic oxide, marsh-gas, empyreumatic oil, and charcoal.

Mucic acid is resolved into 2 At. carbonic acid, 6 At. water, and Pyromucic acid:

$$C^{12}H^{10}O^{16} - 2CO^2 - 6HO = C^{10}H^4O^6.$$

Citric acid, when heated in a retort, gives off 2 At. water, and leaves a residue of Aconitic acid:

$$C^{12}H^8O^{14} - 2HO = C^{12}H^6O^{12}.$$

This aconitic acid, if more strongly heated in the retort, gives off 2 At. carbonic acid, and distils over as Itaconic acid:

$$C^{12}H^6O^{12} - 2CO^2 = C^{10}H^6O^8.$$

At the same time, another portion of the citric acid is decomposed in a different manner, being resolved into carbonic oxide, acetone, empyreumatic oil, and charcoal.

Gallic acid, heated to 210°, yields carbonic acid and a distillate of Pyrogallic acid:

$$C^{14}H^6O^{10} = C^{12}H^6O^6 + 2CO^2;$$

but at 250° it gives off water and carbonic acid, and leaves Metagallic acid:

$$C^{14}H^6O^{10} = C^{12}H^4O^4 + 2HO + 2CO^2.$$

Meconic acid gives off carbonic acid, and yields a sublimate of Pyromeconic acid:

$$C^{14}H^4O^{14} = C^{10}H^4O^6 + 4CO^2.$$

Oxalic acid partly sublimes undecomposed; another portion is resolved into water, carbonic oxide, and carbonic acid:

$$C^4H^2O^8 = 2HO + 2CO + 2CO^2;$$

And a third part into formic and carbonic acids:

$$C^4H^2O^8 = C^2H^2O^4 + 2CO^2.$$

A pyro-acid obtained by the dry distillation of another acid, may therefore be regarded as the original acid, deprived of a certain (even) number of atoms of carbonic acid, or of water, or of both together. [*Vid.* Pelouze (*J. chim. méd.* 10, 120; also *Pogg.* 31, 212), whose method of calculating the decomposition-products of organic compounds in general (*Pogg.* 59, 100), we may take this opportunity of noticing.]

Dry distillation is the basis of certain technical operations, especially of the *Preparation of Charcoal* and *Coke*, and the collection and application of the volatile matters thereby produced. In the ordinary process of charring or coaking in heaps or mounds, the greater part of the wood, turf, or coal is subjected to dry distillation by the heat produced by the combustion of the other part in the sparingly admitted air; at the proper time, the fire is put out by excluding the air. In this process, the volatile products of the distillation are lost; the vapours of acetic acid given off in the charring of wood may, however, be condensed, and obtained in the form of acetate of lime, by covering the heap with lime-dust instead of earth. A more complete method of collecting these volatile

products is to heat wood, turf, coal, resin, or bones and other parts of animals, to redness in closed vessels of cast-iron or brickwork, either by means of a furnace surrounding the vessel, or of several furnaces placed within it. The elastic fluids, which issue by a tube from the generating vessel, are made to pass through cooler spaces, where they deposit their tar and watery liquid, while a mixture of combustible gases remains uncondensed. The charring of wood, conducted in this manner, yields chiefly *Wood-vinegar*, or *Pyroligneous acid*, fitted for the preparation of the purer acetic acid and of wood-spirit; coal, and more especially animal substances, yield large quantities of ammoniacal salts, which are used for the preparation of *Sal-ammoniac* (II., 478). The mixture of uncondensed gases, when freed by milk of lime from carbonic acid and sulphuretted hydrogen, serves for *Gas-lighting*. For the latter purpose, the gas from wood, which contains large quantities of carbonic oxide and hydrogen, and no olefiant gas, is least adapted; that from turf is better adapted; still better that from coal and animal substances, which contains olefiant gas; better even than this is the gas from resin; and the greatest quantity of light for a given volume, is yielded by the gas produced by dropping fatty substances into tubes kept at a dull red heat, this gas being particularly rich in olefiant gas, and likewise in the vapour of two empyreumatic oils, and one empyreumatic camphor.

Disinfecting power of Heat.—The poison of cow-pock retains its efficacy when dried in the air on a glass plate at ordinary temperatures, and then heated for four hours to 49°, but becomes innocuous if heated for four hours to a temperature between 54·5° and 60°; hence 54·5° appears to be the limit. Woollen jackets which have been worn by persons suffering from a contagious typhus or scarlet fever, if exposed to a heat of 95·4°, do not communicate the contagion to healthy persons. Hence bales of cotton suspected of the plague, should be opened and heated in double leaden receivers, by surrounding them with aqueous vapour; it is true that the cotton then becomes very brittle from loss of water, but its tenacity may be restored by exposure to the air. (W. Henry, *Phil. Mag. Ann.* 10, 363; 11, 22, and 205.) It is not yet decided whether this action depends upon the destruction of certain organisms of the lower orders and their germs, or on the decomposition of poisonous organic compounds, either by heat alone, or by the simultaneous oxidizing action of the air. (Gm.)

b. A still more complete transformation of organic compounds takes place when, instead of being gradually heated to redness, they are suddenly exposed to a red heat by passing them through a red-hot tube. The oxygen of the organic compound is then, in most cases, completely converted into carbonic oxide, carbonic acid, and water; the hydrogen not thereby consumed, partly escapes as gas, partly unites with the carbon to form gaseous, oily, and camphoroidal compounds, and partly with the nitrogen to form ammonia. But the stronger and more continued the heat to which the vapour is exposed (by using a long tube, and passing the vapour through it slowly), the more completely are the hydrocarbons resolved—since the affinity of heat for hydrogen increases with the temperature—into pure hydrogen, and carbon which is deposited in the form of soot; in a similar manner, carbonate of ammonia, especially if the tube contains fragments of porcelain or metal wire (II., 432), is resolved into hydrogen, nitrogen, and carbonic acid or carbonic oxide gas.

Naphthalin, $C^{20}H^8$, is not directly produced in the dry distillation of coal, but only when the volatile decomposition-products are passed through a hotter part of the apparatus, and thereby undergo a further decomposition; one of the products then formed is naphthalin. (Reichenbach, *Schw.* 61, 175.) As the cast-iron retorts in which coal is distilled for gas-lighting, are ultimately heated to redness, the carbon derived from the volatilized hydrocarbons is deposited in their inner surfaces, in the form of graphitic scales. (Marchand, *J. pr. Chem.* 26, 482.)

3. *Decomposition by Combustion.*

a. Slow Combustion.—Many organic compounds take up oxygen from the air at the ordinary temperature, or a little above it, and are thereby converted, sometimes into organic compounds richer in oxygen, sometimes entirely into inorganic compounds.

Volatile oils become resinous by exposure to the air; so likewise do certain volatile alkaloids, *e. g.*, nicotine and coniine. Fixed oils become more tenacious or more solid, as is the case with linseed oil. Aldehyde, $C^4H^4O^2$, is converted into acetic acid, $C^4H^4O^4$; acrolein, $C^6H^4O^2$, into acrylic acid, $C^6H^4O^4$; cacodyle, C^4H^6As, when partially exposed to the air, is converted first into oxide of cacodyle, and then into cacodylic acid.

Many compounds which would remain unaltered if simply exposed to the air, take up its oxygen if they are at the same time in contact with large surfaces of platinum, which absorbs oxygen from the air and transfers it to the organic compound (II., 25): Saligenin, $C^{14}H^8O^4$, when heated *per se* in the air, is converted, with formation of water, into salicylous acid, $C^{14}H^6O^4$, but in contact with platinum-black, the conversion takes place at ordinary temperatures.—Platinum-black, moistened with aqueous oxalic or formic acid, causes it to burn away slowly, and form carbonic acid and water. It induces the conversion of hydrated wood-spirit, $C^2H^4O^2$, into formic acid, $C^2H^2O^4$; and of hydrated alcohol, $C^4H^6O^2$, into acetic acid, $C^4H^4O^4$. When stronger wood-spirit, or alcohol, is dropped upon it, the metal becomes heated to redness. To this class of actions also belongs the imperfect combustion of the vapour of alcohol, ether, volatile oils, camphors, &c., which takes place when these vapours, mixed with air, come in contact with platinum foil or wire heated below redness, the metal being thereby raised to a red heat.

b. Rapid Combustion.—Since organic compounds contain less oxygen than is required to convert their carbon into carbonic acid, and their hydrogen into water, they take up, when heated in the air, the oxygen required for that purpose. They then, for the most part, exhibit the phenomena of rapid combustion, which is more vivid as the substances themselves are less rich in oxygen, and also as they contain less nitrogen, inasmuch as that element plays a less active part in the combustion.

Sometimes the combustion begins without the application of any external heat; for some few substances, such as cacodyle and its oxide, take fire at the ordinary temperature of the air. In other substances, when they are exposed to the air in large masses, and with surfaces of considerable extent, the heat developed by slow combustion sometimes goes on accumulating; the combustion is then accelerated, and the temperature again raised thereby; and in that manner the action may go on till the organic body bursts into flame. Sometimes this rise of tem-

perature is assisted by fermentation going on in the interior of the mass.

The following substances have been known to take fire spontaneously: hemp, flax, tow, linen, paper, cotton, wool, ashes, ochre, and other porous substances, when saturated with any fixed oil, especially with a drying oil (*q. v.*). (Rüde, *Taschenb.* 1782, 151); coffee, peas, or beans, tied up in a sack after roasting and grinding; oatmeal, hay, flax, hemp, cotton, turf, dung, horse-dung, for example, when heaped up in the damp state, especially in a warm atmosphere.

The spontaneous inflammation of many kinds of charcoal, arises not so much from slow combustion, as from the development of heat produced by the absorption of air and aqueous vapour (*vid. Charcoal*); that of the pyrophorus from the presence of potassium, &c. (*vid. Pyrophori*); that of coal heaped up in mass and moistened, from the slow oxidation of the white iron pyrites contained in it (V. 232); *comp.* Mohr (*Ann. Pharm.* 35, 339).

On spontaneous combustion in general, *comp.* Thomson (*Ann. Phil.* 16, 390). Froriep's Notizen (1820, No. 140); Mense (*Sill. Am. J.* 38, 147, and 199).

When rapid combustion takes place completely, a compound consisting only of carbon, hydrogen, and oxygen, is entirely converted into carbonic acid and water; a compound containing nitrogen yields nitrogen gas in addition, and frequently also a small quantity of nitric acid.

If the organic compound contains fixed inorganic matters, these are left behind in a more or less altered state in the form of *Ash*. Any compounds of potash, soda, lime, &c., with sulphuric or phosphoric acid, and likewise the corresponding chlorides that may exist in an organic compound, generally remain unaltered after combustion; if, however, the supply of air be deficient, sulphates may be converted into sulphides. But compounds of bases with nitric acid, or with organic acids, are converted into carbonates, and remain as such in the ash. Planché (*J. Pharm.* 23, 545) however maintains that the nitre existing in quassia-wood, may remain unaltered in the ash after the wood is burned.

Rapid combustion is often imperfect. For, while that part of the organic compound which is in immediate contact with air or oxygen gas burns away, the other part not so exposed is decomposed by the heat thereby produced, in the same manner as if it were subjected to dry distillation, or passed through a red-hot tube. If now the combustible mixture of gases, vapours, and soot, thus produced with an insufficient supply of air, be not brought soon enough in contact with the quantity of air necessary to burn it completely, it cools down below its burning point, and mixes in the form of smoke and soot with the ascending air.

When a piece of wood is set on fire, part of it is brought into the condition of dry distillation, and the evolved gaseous mixture burns with a flame which continues to heat the inner portion and liberate volatile substances, till, as in the dry distillation of wood, part of the carbon is left behind in the form of charcoal. That portion of the disengaged vapour which escapes combustion condenses in the chimney in the form of wood-tar and pyroligneous acid, which dry up to a shining soot (*Glanzruss*). The finely divided charcoal deposited in the form of ordinary soot (*Flatterruss*) is not an immediate product of the dry distillation, but is formed in the inner part of the flame; because the combustible vapours are surrounded with a white-hot envelope, which forms the boundary between the combustible vapours and the air, and is consequently the place where the actual combustion goes on; and the vapours are there decomposed in the same

manner as if they were passed through a red-hot tube. [On the combustion and flame of ordinary illuminating materials, *comp.* II, 39.]

Organic compounds may undergo rapid combustion, not only in contact with air or oxygen gas, but likewise by contact with many substances containing oxygen loosely combined. Many organic compounds when raised to a certain temperature in the vapour of perchloric or hyponitric acid, or in nitrous-oxide gas, or in contact with strong nitric acid, take fire and burn with a brighter flame than when they are burned in the air. They exhibit incandescence when heated with iodic or chromic acid, or their salts, also with periodates, bromates, chlorates, perchlorates, nitrites, nitrates, manganates, and permanganates; when intimately mixed with these substances, they often explode with flame, sometimes at ordinary temperatures, sometimes by a blow, sometimes only when heated. They also become incandescent when heated with certain peroxides, such as peroxide of lead, which sets fire to many compounds when triturated with them merely at ordinary temperatures,—also with other metallic oxides, the oxygen in which is but loosely combined, such as teroxide of gold, oxide of silver, and the protoxides of mercury and copper.

Since in all these combustions, when they are so conducted as to be perfect, the whole of the carbon of the organic compound is converted into carbonic acid, and the whole of the hydrogen into water, the quantity of which products can be determined, and the amount of carbon and hydrogen in the organic compound thereby estimated, these combustions serve to determine the per-centage of the carbon and hydrogen in an organic compound; that is to say, for the ULTIMATE OR ELEMENTARY ANALYSIS OF ORGANIC COMPOUNDS.

For this purpose, the organic compound is burned in a tube, called the Combustion-tube, either in a stream of oxygen gas, or intimately mixed with a very large excess of chlorate of potash, oxide of copper, or chromate of lead. The evolved mixture of carbonic acid and vapour of water is first passed through a tube filled with chloride of calcium, or with asbestos moistened with oil of vitriol, the increase of weight in which gives the quantity of water produced; and the carbonic acid is estimated either by receiving it in graduated tubes over mercury, or by connecting the chloride of calcium tube with Liebig's potash-apparatus, in which the whole of the carbonic acid is absorbed by the potash-ley, so that its increase of weight gives the quantity of carbonic acid produced. Since 9 parts of water contain 1 pt. of hydrogen, and 22 pts of carbonic acid contain 6 pts. of carbon, the composition of a hydrocarbon may be easily calculated from the quantities of water and carbonic acid obtained; if the compound likewise contains oxygen, the deficiency gives the proportion of that element. There is no known process by which the quantity of oxygen in an organic compound can be directly estimated.

Nitrogen, when it occurs in an organic compound, must be estimated by a separate experiment, in one of the three following ways: 1. The mixture of the compound with excess of oxide of copper is ignited in a tube, and after the air has been completely expelled, the mixture of carbonic acid and nitrogen is received in a graduated tube. The quantity of gas is then read off; caustic potash introduced to absorb the carbonic acid; and the volume of residual gas, which is nitrogen, also accurately measured. The proportion by volume between the carbonic acid and the

nitrogen is thereby determined; and from this, after the quantity of carbon has been found by an experiment made in the manner already described, the amount of nitrogen is readily calculated.

2. The mixture of the compound with oxide of copper is introduced into the middle of a tube, containing at its closed end, a carbonate, such as carbonate of lead, carbonate of copper, or bicarbonate of soda, from which the carbonic acid may be expelled by heat. The air of the tube is first driven out by heating this carbonate, as well as by exhaustion with the air-pump; the mixture of the organic substance with oxide of copper is then ignited; and the evolved gas is received over aqueous solution of potash, which absorbs the carbonic acid and leaves the nitrogen: lastly, the nitrogen still remaining in the combustion-tube is expelled by again heating the carbonate. This process gives the absolute quantity of nitrogen, the weight being calculated from the observed volume. In both these processes (1) and (2), a quantity of finely divided metallic copper is placed at the open end of the tube, and kept at a red heat, in order to withdraw the oxygen from any nitric oxide or hyponitric acid which may be formed by the nitrogen of the compound taking oxygen from the oxide of copper.

3. The azotized organic substance is mixed with a large excess of *soda-lime* (prepared by fusing hydrate of soda with pounded lime), and the mixture gradually heated to redness in a tube. The whole of the nitrogen is thereby expelled in the form of ammonia, which is absorbed by hydrochloric acid, and precipitated by bichloride of platinum in the form of platinum sal-ammoniac; and, the precipitate having been washed with a mixture of alcohol and ether, the amount of nitrogen in the compound is calculated from its weight.

¶ Nöllner (*Ann. Pharm.* 66, 314) passes the ammonia directly from the combustion-tube into a solution of tartaric acid in absolute alcohol, and estimates the quantity of nitrogen from the acid tartrate of ammonia thereby produced (the salt containing 10·2 p. c. NH^3 or 8·4 p. c. N).—E. Schmidt (*Arch. Pharm.* [2], 50, 317) passes the ammonia, together with a stream of carbonic acid, into a solution of 1 pt. chloride of barium in 8 pts. water; heats the liquid to the boiling point; filters; and calculates the quantity of nitrogen from the weight of the ignited carbonate of baryta thus obtained.

Péligot (*Compt. rend.* 24, 550; *Ann. Pharm.* 64, 402) receives the ammonia in a known volume or weight of sulphuric acid of determinate strength (using for each experiment 100 cub. cent. of an acid containing 61·250 grm. of HO,SO^3 in a litre, so that 100 cub. cent. correspond to 2·12 grm. of ammonia, or 1·75 grm. of nitrogen). The acid containing the ammoniacal salt is poured into a beaker glass, coloured with a few drops of tincture of litmus, and neutralized with a standard solution of lime in *eau sucrée*, the exact point of neutralization being known by the change of colour from red to blue. The volume of the sugar-lime solution required to saturate 10 cub. cent. of the standard acid having been previously determined, the volume of the acid combined with the ammonia (and thence the quantity of nitrogen) is found by deducting the volume of acid which corresponds to the quantity of sugar-lime used after the absorption of the ammonia, from the volume of pure acid taken, viz., 10 cub. cent. [For further modifications of this process, *vid.* Péligot, *Compt. rend.* 24, 1155].—A similar modification of process 3, had previously been proposed by Bineau (*N. J. Pharm.* 11, 462; *Compt. rend.* 24, 686; 25, 254), who, however, recommends a standard solution of

hydrochloric acid instead of sulphuric, and of soda-ley instead of the sugar-lime solution.—Mitchell (*Chem. Soc. Qu. J.* 1, 19) also substitutes for the sugar-lime, a solution of caustic soda of sp. gr. 1·018, and for the tincture of litmus a decoction of Campeachy wood; a few drops of this decoction impart to the acid liquid a yellowish brown colour, which the slightest excess of alkali immediately converts into blackish blue. ¶

Chlorine, bromine, iodine, sulphur, arsenic, &c., when they occur in organic compounds, must be estimated by special processes.

Complete descriptions of the different processes of ultimate organic analysis, are given especially by: Gay-Lussac and Thénard, *Recherches*, 2, 265; also *Gilb.* 37, 4011.—Berzelius, *Lehrbuch der Chemie*, Ausg. 3, 6, 28.—Liebig, *Handwörterbuch*, 1, 357.—Mitscherlich, *Lehrb. d. Chem.* Aufl. 4, 1, 1, 125.—Dumas, *Traité de Chimie appliquée aux Arts*, 5, 4; also in *J. Pharm.* 20, 129.—H. Rose, *Analyt. Chem.* Aufl. 1851, Bd. 2, s. 812, 935, 990.—Regnault, *Cours élémentaire de Chimie*, 4.

Special Processes and Modifications in Ultimate Analysis, alphabetically arranged:

Babington.—Determination of Water. *Quart. J. of Sc.* 19, 182.

Berard.—With oxide of copper. *Ann. Chim. Phys.* 5, 290; also *Schw.* 22, 439; also *N. Tr.* 2, 2, 192.

Berthollet.—The vapours passed through a red-hot tube, and the resulting gaseous mixture analysed. *Mém. d'Arcueil*, 3; also *Schw.* 29, 490.

Berzelius.—Analysis by chlorate of potash. *Ann. Phil.* 4, 323.—By oxide of copper and chlorate of potash together. *Pogg.* 19, 308.—By oxide of copper; moisture therein;—by oxide or chromate of lead, in the case of compounds containing sulphur, in order to prevent the evolution of sulphurous acid. *Pogg.* 44, 389.—Determination of nitrogen by hydrate of potash. *J. pr. Chem.* 23, 231,

Bineau.—Modification of method 3 for the determination of nitrogen, *Compt. rend.* 24, 686 and 1155; 25, 254; *Jahresber.* 1847–8, 955.

Bromeis.—Soda-lime serves for the determination of nitrogen in volatile organic compounds. *Ann. Pharm.* 52, 134.

Brunner.—Combustion in oxygen gas. *Pogg.* 26, 497; 34, 325.—Combustion in air. *Pogg.* 44, 138.

Bunsen.—Determination of nitrogen. *Ann. Pharm.* 37, 27.—Determination of arsenic and mercury. *Ann. Pharm.* 37, 2 and 41.

Chevreul.—Combustion by oxide of copper. *Recherches chimiques sur les corps gras*, 8.

Claus.—Combustion by oxygen gas. *J. pr. Chem.* 25, 256.

Cooper.—With oxide of copper and spirit-lamps. *Ann. Phil.* 23, 170.

Couerbe.—With oxide of copper. *Ann. Chim. Phys.* 52, 352.

Crum.—With oxide of copper. *Ann. Phil.* 21, 85.

Döbereiner.—With oxide of copper. *Schw.* 17, 369; further, *N. Tr.* 2, 1, 357,

Döpping & Schlossberger.—Determination of nitrogen. *Ann. Pharm.* 52, 107.

Dumas.—Determination of nitrogen. *Ann. Chim. Phys.* 44, 133 and 172; 47, 198 and 324 (these two memoirs also in *N. Tr.* 25, 2, 237); 53, 171.

Dumas & Pelletier.—With oxide of copper. Determination of nitro-

gen. *Ann. Chim. Phys.* 24, 163 and 187; also *Schw.* 40, 76; also *Kastn. Arch.* 1, 385; also *N. Tr.* 9, 1, 129.

DUMAS & PIRIA.—Antimonious acid with potash-compounds. *N. Ann. Chim. Phys.* 5, 365 and 366.

DUMAS & STAS.—Exact determination of carbon. *Ann. Chim. Phys.* 76, 38; *N. Ann. Chim. Phys.* 1, 38.

ERDMANN.—Chloride of calcium after fusion for a short time does not absorb carbonic acid. *J. pr. Chem.* 13, 424.—Protection of the cork between the combustion-tube and the chloride of calcium tube, with lead-foil. *J. pr. Chem.* 13, 513.—Combustion in oxygen gas, 19, 322.—Absorption of oxygen gas by the potash-ley, 22, 258.

ERDMANN & MARCHAND.—Determination of nitrogen. *J. pr. Chem.* 14, 206; 22, 148.—Combustion in oxygen gas, 23, 175; 27, 129.

FELLENBERG.—Potash-compounds burnt with oxide of copper. *Pogg.* 44, 447.

GAY-LUSSAC.—Analysis with oxide of copper. *Ann. Chim.* 96, 306; also *Schw.* 16, 84; further, *J. Pharm.* 8, 581; also *Repert.* 15, 184.

GAY-LUSSAC & LIEBIG.—Analysis of fulminating silver. *Ann. Chim. Phys.* 25, 290.

GROS.—Analysis of compounds containing chlorine. *Ann. Pharm.* 27, 243.

O. HENRY & PLISSON.—Peculiar method. *J. Pharm.* 16, 249 and 581; 17, 437; 18, 285; 19, 16; 20, 54.

HERMANN.—Analysis of rock-oil. *Pogg.* 18, 386.

HESS.—Determination of hydrogen. *Pogg.* 43, 577; also *Ann. Pharm.* 26, 189.—Analysis by oxygen gas. *J. pr. Chem.* 17, 98; also *Pogg.* 46, 179;—further, *J. pr. Chem.* 17, 399; *Pogg.* 47, 212.

LAURENT.—Method of determining hydrogen within $\frac{1}{1000}$ of the whole. *N. Ann. Chim. Phys.* 19, 360; *Ann. Pharm.* 62, 96; *J. pr. Chem.* 490; *Jahresber.* 1847—8, 942.

LERCH.—Analysis of baryta-compounds with oxide of copper. *Ann. Pharm.* 49, 216.

LIEBIG.—Nitrogen-determination, &c. *Pogg.* 17, 391; 18, 357.—Nitrogen-determination and potash-apparatus. *Pogg.* 21, 1.—Analysis of chlorine-compounds. *Pogg.* 24, 261.—Desiccation of the compounds to be analysed; Nitrogen-determination. *Pogg.* 27, 679.—Determination of hydrogen. *Ann. Pharm.* 26, 192.

LIEBIG & WOHLER.—Analysis of sulphovinates. *Pogg.* 22, 486.—Drying of the mixture in the combustion-tube. *Pogg.* 26, 330.—Introduction of peroxide of lead before the chloride of calcium-tube, in the analysis of sulphur-compounds, to absorb the sulphurous acid. *Ann. Pharm.* 26, 270.

LÖWIG.—Determination of the sulphur in organic compounds by ignition with nitre and carbonate of baryta.

MAGNUS.—Evaporation of water from the potash-apparatus. *Pogg.* 40, 587.

MALLET.—Galvanic coating of the combustion-tube with a film of copper. *Phil. Mag. J.* 22, 439.

MANZINI.—Determination of nitrogen. *N. J. Pharm.* 2, 98.

MARCHAND.—Water proceeding from the cork of the combustion-tube; peculiar arrangement of the potash-apparatus. *J. pr. Chem.* 13, 409.

MELSENS.—Determination of nitrogen. *Compt. rend.* 20, 1437.

MICHAELIS.—Determination of nitrogen. *Schw.* 25, 461.

MITCHELL.—Determination of nitrogen by method 3. *Chem. Soc. Qu. J.* 1, 19; *Jahresber.* 1847—8, 956.

MULDER.—Analysis of nitrogen-compounds and of non-pulverizable, fibrous substances. *Pogg.* 40, 213 and 266.—Analysis of compounds containing sulphur and phosphorus. *J. pr. Chem.* 15, 190.—Combustion of mould by oxide of copper and chlorate of potash. *J. pr. Chem.* 21, 206.

MULDER.—Observations on Dumas' method of determining nitrogen. *Pharm. Centrb.* 1849, 508; *Jahresber.* 1849, 577.

NÖLLNER.—Determination of nitrogen by method 3. *Ann. Pharm.* 66, 314; *Jahresber.* 1847—8, 956.

OPPERMANN.—Analysis of oil of turpentine. *Pogg.* 22, 196.

PÉLIGOT.—Determination of nitrogen by method 3. *Compt. rend.* 24, 550; *N. J. Pharm.* 11, 334; *J. pr. Chem.* 41, 122; *Ann. Pharm.* 64, 402; *Jahresber.* 1847—8, 954.

PERSOZ.—Analysis by means of mercuric sulphate. *Ann. Chim. Phys.* 75, 5.

PFAFF.—Analysis of nitrogenous bodies. *Schw.* 61, 494; 62, 42.

PROUT.—Peculiar apparatus for analysis by oxide of copper. *Ann. Phil.* 15, 190; also *Schw.* 29, 487.—Peculiar apparatus for combustion by oxygen gas. *Phil. Trans.* 1827, 355; also *Schw.* 53, 218.

REISET.—Determination of nitrogen. *Compt. rend.* 15, 134; further, *N. Ann. Chim. Phys.* 8, 232.

RICHARDSON.—Analysis of coal by oxide of copper; determination of the nitrogen contained in it; analysis by chromate of lead. *Ann. Pharm.* 23, 44 and 58.

RIGG.—Peculiar process. *Phil. Mag. J.* 12, 31, and 232.

H. ROSE.—Potash-apparatus connected with a tube containing hydrate of potash. The oxygen absorbed by the potash-ley may be expelled by a current of air. *Pogg.* 48, 66.

H. SAUSSURE.—Combustion in oxygen gas. *Bibl. Brit.* Nos. 448, 333.

SCHMIDT.—Determination of nitrogen by method 3. *Arch. Pharm.* [2], 50, 317; *Jahresber.* 1847—8, 956.

SCHRÖTTER.—Analysis by oxide of copper in a peculiar tube. *Zeitschr. Phys. v. W.* 4, 21.

SERULLAS.—Analysis by oxygen gas, in a manner similar to that of Prout. *Ann. Chim. Phys.* 39, 182.

URE.—Analysis by oxide of copper in a peculiar apparatus. *Phil. Trans.* 1822, 457.

VARRENTRAPP & WILL.—Determination of nitrogen by method (3). *Ann. Pharm.* 29, 257; 45, 95.

WÖHLER.—Sesquioxide of manganese instead of peroxide of lead for absorbing the sulphurous acid gas evolved from compounds containing sulphur. *Ann. Pharm.* 50, 13.

ZEISE.—Analysis of sulphur-compounds. *Pogg.* 31, 411; 35, 490, and 495.

——— Analysis of chlorine-compounds. *Pogg.* 40, 245.

4. *Spontaneous Decomposition.*

This term is applied to decompositions of organic bodies either simple or complex, taking place at ordinary temperatures, and produced merely by the action of air and water. For most of these decompositions, both

air and water are required, and only a small number of organic compounds are susceptible of them.

Spontaneous decomposition consists either in a slow combustion of the organic matter by the surrounding air, or in a new arrangement of the elements of the compound in different proportions, and the consequent formation of new products. The former process, that of slow combustion, may be called *Eremacausis* or *Decay* (*Verwesung*); the latter, *Fermentation* or *Putrefaction in the widest sense* (*Gährung oder Fäulniss im weitesten Sinne*). When the latter process of inward decomposition is accompanied by an offensive odour, which is particularly the case with nitrogen and sulphur compounds, it is denoted by the special term *Putrefaction* (*Fäulniss*); in the contrary case, especially if it yields useful products, it is called *Fermentation* (*Gährung*). Both processes, viz., that of slow combustion and that of inward decomposition, generally take place simultaneously. An abundant supply of air is favourable to the former, a scanty supply to the latter; hence decay takes place most on the surface, fermentation in the interior of the mass. Many substances are more inclined to decay, others rather to fermentation.

Eremacausis or *Decay.* A slow combustion taking place in presence of air and water, and accompanied by a fermentation-process. The water doubtless acts in this process in the same manner as in the rusting of iron, viz., by absorbing the oxygen of the air and transferring it, in the liquid form, to the constituents of the organic compound.

Simple oxidation of organic substances in the air, such as the conversion of aldehyde into acetic acid, or the resinizing of volatile oils by exposure to the air (p. 84), must not be regarded as instances of eremacausis.

In eremacausis or decay, the carbon and hydrogen of the compound are converted by combustion into carbonic acid and water, and the nitrogen either escapes in the form of gas, or is converted into nitrous and nitric acid. As in this process, the compound continually loses more and more carbon and hydrogen, it might be supposed that the residue would become continually richer in oxygen. This, however, is not always the case. For, while the carbon of the compound is combining with the oxygen of the air and forming carbonic acid, it is possible that a large portion of the oxygen contained in the compound may go off with the hydrogen in the form of water, so that the residue may become richer in carbon than the original compound. Such, according to Saussure, is the process which takes place in the decay of wood and its conversion into humus or mould, a substance which is richer in carbon, but is afterwards, by a further process of decay, completely converted into carbonic acid and water.

A decaying substance may bring other bodies into the state of slow combustion. Decaying organic substances surrounded with a mixture of hydrogen gas and air or oxygen, cause it to condense in the form of water. (Saussure, *comp.* II., 57.) Decaying substances in contact with water and alcohol cause the latter substance to oxidize and form acetic acid. (Liebig.)

Eremacausis is accompanied by *Evolution of Heat*; which in most cases, in consequence of the slowness with which it takes place, and the cooling produced by surrounding objects, amounts to only a few degrees, but when large masses are concerned, may, under favourable circumstances, rise to such a height as to induce rapid combustion (p. 85);

e. g., the smoking of dung. In some few cases, eremacausis is attended with *Development of Light*, as in decaying wood, &c. (II., 28.)

With regard to the behaviour of nitrogen in eremacausis, a great number of particulars have to be observed.

1. The nitrogen of an organic compound escapes in the form of gas, especially if the air has free access, or the compound is exposed to the sun, and no salifiable bases are present.

2. It is converted into nitric acid, especially with free access of air, in the shade, and in presence of a salifiable base, which favours the formation of the nitric acid by predisposing affinity. (II., 388; III., 68.) This base may be potash, soda, lime, or magnesia, in combination with carbonic acid or a vegetable acid; for the carbonic acid escapes as fast as the nitric acid comes in contact with the potash, and the organic acid is destroyed by the slow combustion. The ammonia produced by fermentation in the interior of the mass may also, when it reaches the surface, induce the oxidation of the nitrogen which is there being set free, and form nitrate of ammonia by combining with it, as was formerly observed by Thaer and Einhof in the putrefaction of cow-dung. If fixed salifiable bases are present, the nitrogen of the ammonia itself may also be oxidized and converted into nitric acid. (Kühlmann; II., 388.) According to Vaudin's experiments (*vid. inf.*), the formation of nitric acid appears to be preceded by that of nitrous acid.

3. The nitrogen of the compound unites with its hydrogen and forms ammonia, which generally escapes as carbonate. This ammonia is not so much a product of eremacausis as of fermentation.

4. Non-azotized organic compounds appear, under certain circumstances, to absorb nitrogen from the air during eremacausis, either in the form of ammonia or of nitrous acid.

Extract of *Hyoscyamus*, when kept for a long time, forms carbonate of ammonia in the interior of its mass, but becomes covered on the surface with needles of nitrate of ammonia. (Flashoff, *N. Tr.* 11, 2, 134.)

The leaves of mangel-wurzel grown on a poor, sandy soil do not contain any perceptible quantity of nitre (those which grow on a rich soil contain a considerable quantity), but chiefly malate and oxalate of potash. But when suspended on threads for some months, they become thoroughly penetrated with nitre and covered with fine crystals, nitric acid having in fact been formed by decomposition of the azotized matter in the leaves; the oxalate and malate are found to have disappeared entirely. (Braconnot, *Ann. Chim. Phys.* 35, 261; also *Pogg.* 10, 506.)

Extract of quassia, after a year's exposure to the air, contains more nitre than it would contain if kept for the same time in close vessels. (Planche, *J. Pharm.* 23, 548.)

Extract of *Borago off.* when not sufficiently evaporated, gives off nitric oxide gas on being stirred. (Guibourt, *J. Pharm.* 12, 134.)

The aqueous infusion of orange-leaves evaporated in the air on flat dishes, yields, according to Vaudin, an extract which, if exposed for a few hours to damp air, and then collected in a pot, swells up considerably, from evolution of nitrous acid, and continues for some months to give off this gas, whenever it is stirred. A similar decomposition is observed in the aqueous infusions or decoctions of the following vegetable matters, when they are evaporated in flat dishes, then exposed to moist air, and then further evaporated: *Glycyrrhiza glabra* (dried roots), *Phaseolus vulgaris* (husks dried on the plant), *Vicia faba* (stalks, leaves, and

husks, after drying), *Trifolium pratense* (the dried herb), *Guajacum off.* (bark), *Quassia amara* (wood), *Althæa off.* (roots), *Tilia europæa* (leaves, after a month's drying), *Brassica oleracea* (dead leaves), *Chelidonium majus* (herb, after a month's drying), *Sanicula europæa* (herb, kept for a long time), *Sambucus nigra* (old flowers), *Cinchona* (*Kalisaya-China*), *Vinca minor* (leaves and flowers, dried for a month), *Datura Stramonium* and *Solanum nigrum* (the herb of both, dried for a month), *Cynoglossum off.*, *Borago off.*, *Lycopsis arvensis* (the herb of all three, dried for a month), *Glecoma hederaceum* (herb and flowers, kept for a long time), *Verbascum Thapsus* (leaves withered on the stem), *Helianthus annuus* (withered leaves), *Salix alba* (old bark), *Populus nigra* (old bark), *Populus tremula* (withered leaves, decayed wood, saw-dust), *Ulmus campestris* (fallen leaves), *Quercus robur* (very old tan) *Corylus avellana* (leaves, dried for a month), *Pinus Abies* (old bark), *Cannabis sativa* (old leaves), *Asparagus off.* (herb with berries), *Scilla maritima* (the powdered root exposed to the air for three months), *Juncus conglomeratus* (withered herb), *Secale cereale* (roots, haulm, empty ears, grain, straw from thatch, both the lower part and that which has been exposed to the air), *Triticum æstivum*, *Avena sativa* (the green plant of both, dried for a month), *Hordeum vulgare* (haulm and ears), *Lichen islandicus* (dried for a month), *Polypodium Filix mas* (roots exhausted with water and alcohol, and then exposed to the air), *Polypodium Filix femina* (the green leaves dried for a month). These vegetable matters must, however, be exposed to the air for some weeks, before they will yield any traces of nitric oxide. This gas is evolved, sometimes on merely stirring the extract, sometimes when it is in smaller quantity, on the addition of tartaric acid, which, if the extract merely contains nitre, does not liberate nitric oxide. The juice of fresh plants never gives off nitrous vapours when treated with tartaric acid. The formation of nitrous acid in vegetable matters takes place much more quickly in damp than in dry air. The air yields both nitrogen and oxygen for the formation of the nitrous acid (Vaudin). [Saussure (*Bibl. Univ.* 56, 130) rightly observes that the nitrogen might also be derived from an azotized compound in the plant.]

It appears to be the woody fibre of plants which more especially attracts the nitrogen of the air; and the nitrogen thus absorbed takes up oxygen and remains combined with the woody fibre in the form of nitrous acid, till that acid is transformed into nitric acid, which then unites with the potash and lime contained in the salts of the vegetable acids present. When liquorice-wood is exhausted 22 times, first with cold and then with hot water, the last extract still gives off nitrous fumes when treated with tartaric acid. The juice expressed from the fresh herb of *Lycopsis arvensis* contains neither nitrous acid nor nitre; but the exhausted residue, after four weeks' exposure to the air, yields with hot water an extract which gives off nitrous acid when treated with tartaric acid, and deflagrates on red-hot coals. When Iceland moss (*Lichen islandicus*) is several times exhausted, first with cold and then with hot water, and exposed to the air for some time after each immersion, all the extracts yield nitrous acid and nitre. (Vaudin, *J. chim. méd.* 1, 674; 9, 321.)

Connected with the above, but not sufficiently explained, are the following observations, in which, however, the evolution of nitric oxide gas must be regarded as a consequence of fermentation: Wood-leaves gave off nitric oxide after two or three days' fermentation. (Chevallier.) The herb of wormwood, pressed into a still containing water, and distilled on the following day, gave off nitric oxide at the commencement

of the distillation. (Tilloy.) The same gas was evolved in the fermentation of mangel-wurzel juice, to which no sulphuric acid had been added. (Derosne.) When syrup from the preparation of beet-sugar, which contained no free acid, but on the contrary, carbonate of ammonia, was diluted with water and mixed with beer-yeast, it scarcely began to ferment and give off carbonic acid, when nitric oxide gas was also evolved and checked the fermentation. But on diluting it with twice the quantity of water, adding a sufficient quantity of sulphuric acid to produce a slight acid reaction,—whereupon a large quantity of carbonic acid was given off,—heating the liquid for a quarter of an hour to the boiling point, which produced no evolution of nitric oxide,—then cooling it and adding yeast, it passed completely into the state of vinous fermentation, without giving off nitric oxide. (Tilloy, *J. Pharm.* 12, 123.)

When the air has but partial access, part of the hydrogen of the organic compound appears to combine with the nitrogen of the air and form ammonia, which can then supply the requisite quantity of nitrogen to the fungi which grow upon these putrefying substances.

If an aqueous solution of milk-sugar or common sugar be left for three months in a stoppered bottle, together with a sevenfold volume of air, and the mould, which is produced in particular abundance from the milk sugar, be subjected to dry distillation, a large quantity of ammonia is obtained; hence there has been produced in the fungus, together with cellulose (woody fibre) a nitrogenous substance, which is doubtless protein; for when the fungus produced from milk sugar is digested in acetic acid, a liquid is obtained which gives a precipitate with ferrocyanide of potassium.—Starch from arrow-root, when kept under water in a bottle also containing air, soon becomes very turbid, and in ten weeks forms a white deposit, together with a large quantity of mould in the mass, and finally also a little on the surface. A fungus of this kind obtained from potato-starch yielded strong traces of ammonia when subjected to dry distillation.—A mixture of humic acid and sugar, moistened with a small quantity of water, and kept for six months in a closed vessel containing air, gives off a large quantity of ammonia when treated with potash.—Well-ignited charcoal, introduced while still hot into a bottle containing air, and shut up therein for six months in the summer in contact with water and common sugar, milk-sugar, gum-arabic, or potato-starch, gives off ammonia when treated with potash, the quantity being particularly large when milk-sugar is used. [These experiments are not conclusive, because the charcoal may contain cyanide of potassium. *Gm.*] In a similar manner, woody fibre, which putrefies with scanty access of air in the lower strata of a vegetable soil, appears to form ammonia, part of the hydrogen of the wood combining with the oxygen of the air and another portion with the nitrogen. This ammonia, according to Kuhlmann's supposition (II. 387), may be afterwards transformed into nitric acid. In this manner we might explain the formation of nitre in the caves of Zeilan described by J. Davy, where no animal substances can be discovered [there are, however, nitrogenous vegetable matters present]; also the formation of nitre in India, Spain, Egypt, in the grottos on the banks of the Seine, and in many cellars. (Mulder, *J. pr. Chem.* 32, 326 and 344.)

Damp wood, putrefying in confined air, converts the oxygen of the air into an equal volume of carbonic acid gas, producing, at the same time, much more water than carbonic acid. (Saussure.) At the same time, however, a small quantity of nitrogen is absorbed from the air, and

some of it is converted into ammonia, while the remainder enters as nitrogen into the nitroline which is formed together with other fungoid substances. (Hermann, *J. pr. Chem.* 27, 165.) For further details, *vid. Woody Fibre.*

Many organic compounds do not undergo slow combustion at ordinary temperatures or in the dark, but exhibit that phenomenon when moderately heated or exposed to light, especially to direct sunshine.

Air is necessary as well as heat; substances which, between 100° and 120°, suffer no alteration out of contact of air, decompose in the air even when but slightly heated. (Chevreul, *Analyse organique*, 69.)

Compounds which remain unaltered when exposed to the air at medium temperatures in the dark, become changed when likewise exposed to light.

These changes due to the action of light are especially conspicuous in many organic colouring matters, which are bleached thereby.

In the following experiments of Chevreul, coloured fabrics were exposed to sunshine for two years in different media.

1. In vacuo: Indigo, safflower, and orchil remain permanent on wool, silk, and cotton; roucou on silk and cotton; sulphindigotic acid on silk; but roucou on wool, sulphindigotic acid on wool and cotton, and turmeric, as well as Prussian blue, lose their colour on all three of these fabrics. [Either oxygen is not required for this discolouration, or the vacuum was imperfect.]

2. In perfectly dry air: Indigo remains permanent on wool and cotton, less so on silk; sulphindigotic acid stands tolerably well on silk, less on wool and cotton; orchil on wool and silk is nearly destroyed, leaving only a reddish tinge, and on cotton completely; roucou on wool retains its red colour tolerably well; on silk it changes to pale reddish yellow, and on cotton it is completely decolorized. Turmeric and safflower are completely destroyed on all three fabrics. Prussian blue bleaches slightly on cotton, more upon wool and silk.

3. In a vessel exhausted of air and filled with aqueous vapour: Safflower on cotton merely acquires a faint violet tinge; on wool and silk it remains unaltered. Orchil remains permanent on wool and silk, but not upon cotton; turmeric and roucou fade upon cotton; Prussian blue on cotton bleaches more quickly than in vacuo.

4. In air saturated with watery vapour: Indigo on wool,—orchil, saffron and Prussian blue on all three fabrics,—turmeric and roucou on silk and wool, stand as well as in perfectly dry air; but indigo on cotton, sulphindigotic acid on all three fabrics, and turmeric and roucou on cotton, are much more quickly decolorized than in dry air.

5. In the open air: The effects are similar to those in (4).

6. In dry hydrogen gas: Similar effects to those in vacuo.

7. In hydrogen gas saturated with aqueous vapour: The same as in aqueous vapour alone. (Chevreul, *Ann. Chim. Phys.* 66, 71.)

Fresh flowers exposed to sunshine under colourless glass, exhibit the following charges: *Rosa gallica:* quickly turn as pale as those of *Rosa centifolia*, but retain their perfume.—*Viola odorata:* rapid decoloration and browning.—*Malva sylvestris:* quickly turn light brown; afterwards dark brown.—*Verbascum Thapsus:* soon lose their colour and aroma, then swell up, agglomerate together, and afterwards crumble to a brown powder, having an ammoniacal odour.—*Calendula officinalis:* pale yellow colouring.—*Tussilago Farfara:* brown colouring somewhat rapidly pro-

duced, afterwards fermentation.—*Gnaphalium dioïcum:* the colour remains undiminished.—*Convallaria majalis:* the white colour soon changes to light brown, without further alteration. (Langlois, *Bull. Pharm.* 3, 88.)

The aqueous or alcoholic tincture of carnations loses its colour under blue glass in sunshine; so likewise does paper or cotton coloured with it; but in the dark, even at 50°, the paper or cotton so coloured remains unaltered. Alcoholic tincture of saffron is likewise decolorized when exposed to light, whereas that of red sandal-wood and of China stands tolerably well.—The yellow oils of peppermint and savine become colourless on exposure to sunshine; blue oil of camomile and colourless oil of turpentine turn yellow.—When water distilled over aromatic plants [solution of a volatile oil in water] is exposed to the sun for some months in closed glass vessels, the solutions obtained with roses and savine remain clear; but those produced from peppermint, thyme, and fennel become milky, but without reddening litmus more than before. (A. Vogel, *J. Pharm.* 1, 109.)

To this head likewise belongs the decoloration of linseed-oil in sunshine.

Coloured fabrics which gradually fade on exposure to sunlight, suffer the same change in an hour or two when subjected in the dark to a heat between 160° and 200°, the air having access to them at the same time. The following experiments were made with silk stuffs coloured rose-colour by safflower, and with woollen stuffs coloured violet by Campeachy wood, red by logwood, and yellow by weld and turmeric, the colours being in all cases fixed by an alum-mordant. The coloured stuffs were placed in a siphon-shaped tube and immersed in a bath of mercury heated to a certain temperature, the legs of the tube projecting above the mercury, in order that fresh air might be introduced from time to time.

The stuff coloured with safflower remained unaltered after an hour's heating to 120°, but became dirty white in an hour at 160°.—The stuff dyed with Campeachy was but slightly altered in an hour at 150°, but became red-brown in an hour at 180°.—The stuff dyed with logwood remained unaltered for 2 hours at 140°, but became much paler when heated for the same time to 190°.—The stuff coloured with weld was not altered in 2½ hours at 160°, but became more reddish yellow when heated for the same time to 200°. The stuff coloured with turmeric underwent but little change when heated for 1½ hour to 150°, but in the same interval at 200°, its orange-yellow colour changed to rusty brown.—When air saturated with moisture was passed through the bent tube, the changes of colour took place much more quickly. These changes of colour produced by heat are exactly the same as those produced in longer time by light, and in both cases the stuff becomes rotten. Hence they appear to depend upon slow combustion. (Gay-Lussac & Thénard, *Recherches*, 2, 166.)

Yellow resin of guaiacum reduced to powder or diffused through paper (by saturating the paper with an alcoholic solution of the resin and then drying it) acquires a green colour, when exposed to light and at the same time to air, but not in a vessel filled with carbonic acid gas; hence light induces a slow oxidation. (Wollaston, *Gilb.* 32, 291; *comp.* also I., 171.)

Fermentation (including putrefaction) depends, like dry distillation, on an alteration of arrangement of the elements already contained in the

organic compound: but the elements of water are likewise concerned in the action; in fact, without their presence no fermentation can take place. —For the commencement of fermentation, free access of air is often necessary, but when once set up, it can go on without contact of air. (Gay-Lussac.)

In the process of fermentation, organic compounds of a higher order are resolved, sometimes into lower organic compounds, sometimes into inorganic compounds, as carbonic acid, water, ammonia, or sulphuretted hydrogen, sometimes into simple substances, as hydrogen and nitrogen gases. In many fermentations, none of the above-mentioned gases are evolved; in fact, they go on without any evolution of gas. The affinities which tend towards the formation of organic compounds of a lower order, or of inorganic products, are doubtless stronger than those by which the original substance is held together; and this circumstance is doubtless connected with the evolution of heat which accompanies fermentation, and may be partly the cause of the spontaneous combustion of organic bodies.

Fermenting substances generally have a tendency to abstract oxygen from the air and other bodies. Hence, when fermentation takes place with free access of air, it is accompanied by eremacausis on the surface of the organic substance.—Putrefying substances reduce sulphide of iron from ferrous sulphate (V., 228). The conversion of blue into white indigo by the action of grape-sugar in the *indigo-vat* is a process of the same nature.

The substances most disposed to fermentation are numerous compounds rich in nitrogen, viz., the albuminous or protein substances, such as albumen, fibrin, casein, emulsin, legumin, gliadin, gluten, &c., and gelatinous substances, such as membranes consisting of gelatin and other tissues, glue, chondrin, osmazome, &c. On the other hand, there are other compounds rich in nitrogen, such as uric acid, the alkaloids, indigo, &c., which, of themselves, at least, are not capable of putrefying, and even some substances belonging to the class of protein-compounds, but of a coherent nature, such as hair, horn, and hard-boiled albumen, are susceptible only of a slow decay. The former compounds, on the contrary, require only the presence of water and the access of air at the commencement, to bring them into a state of fermentation, which, on account of the offensive odour which accompanies it, is especially denoted by the term putrefaction. Since animals are mainly composed of these substances, they are especially liable to this putrid decomposition; but many seeds of plants, mosses, &c., which are likewise rich in protein-compounds, are also liable to pass into the state of stinking putrefaction. The bad smell which accompanies stinking putrefaction, proceeds partly from inorganic compounds, such as sulphuretted hydrogen and ammonia, partly from newly formed volatile organic compounds, the nature of which is not exactly known. [Respecting the pernicious action of the exhalations of putrefying substances, *comp.* II., 414, 415.]

Of other organic compounds, there are but few which are brought into a state of fermentation by contact with air and water, so long as gelatin and protein-compounds are excluded. Urea dissolved in a very large quantity of water is very slowly resolved into ammonia and carbonic acid; dilute aqueous solutions of many vegetable acids, and more especially of their ammoniacal salts, also of sugar, gum and starch, are decomposed, with formation of mould.

But many substances incapable of fermenting *per se*, undergo that

change when in contact with gelatinous or protein compounds; and those which are capable of fermenting alone, ferment more quickly, or with formation of different products, when they are brought in contact with these compounds. Many compounds, however, those, namely, which consist wholly of carbon and hydrogen, are incapable of fermenting even under these circumstances. As gelatinous and protein compounds excite fermentation in other substances, they are called *Ferments*, and the compounds which are brought into the fermenting state by contact with them are called *Fermentable Substances;* strictly speaking, however, the most fermentable of all substances are the ferments themselves.

Protein- and gelatin-compounds sometimes excite fermentation in other substances, even when they are in the fresh state, as they exist in plants and animals;—sometimes, on the contrary, they must be exposed to the air, so as to bring them into a state of incipient fermentation, before they will act as ferments upon other bodies; and, in this case, it is often found that they will bring another substance into different states of fermentation, according to the particular stage of decomposition which they have themselves attained.

The aqueous solution of salicin or amygdalin would probably remain unaltered for a long time, if left to itself; but the emulsion of almonds (*Synaptase*) added in its unaltered state, just as it exists in recently prepared sweet almond milk, decomposes salicin into grape-sugar and saligenin, and amygdalin into grape-sugar, bitter-almond oil and hydrocyanic acid.—In black mustard, the addition of water induces the formation of volatile oil of mustard, in consequence of the action of the emulsin-like substance contained in it on the myronic acid which it also contains.

Fixed oils appear to pass into a state of rancid putrefaction, only when a protein-compound is mixed with them.

Starch boiled to a paste with water, and then left to itself in a close vessel for some weeks, is in great part converted into grape-sugar, with evolution of carbonic acid and hydrogen; but in contact with gluten at 60°, the starch of the paste is converted into grape-sugar in eight hours; lastly, if the gluten has previously passed into that peculiar condition in which it exists as germinated gluten or *diastase* in malt, it effects this conversion of the sugar at 60° in less than an hour.

A dilute aqueous solution of grape sugar or common sugar, which remains unaltered when alone, or only forms a little mould and mucus after a long time, may be brought, according to the nature of the ferment and its stage of decomposition, and according to the temperature and dilution of the solution, into three different states of fermentation; whereby it is converted: first, into lactic, and then into butyric acid (*Lactic* and *Butyric Acid Fermentation*),—or into a mucous substance allied to gum, and generally at the same time into mannite (*Viscous* or *Gummy* and *Mannite Fermentation*),—or it is resolved into carbonic acid and alcohol (*Vinous Fermentation*). [A solution of milk-sugar undergoes similar changes under some of the following circumstances.]

With beer-yeast or wine-yeast, which may be regarded as ferment in its most perfect state, a solution of sugar passes at once into the state of vinous fermentation. So long, however, as the glutinous matter continues in the unaltered state in which it exists in solution, together with grape-sugar, in the juice of grapes and other fruits, it is not capable of inducing the vinous fermentation; it must first be brought into the state of wine-ferment by contact with a small quantity of air.

When this change has once taken place, the vinous fermentation goes on, even when further access of air is completely prevented. Hence the fruit remains unaltered, so long as its outer skin is uninjured; but a very slight perforation is sufficient to induce the vinous fermentation, which soon extends from the injured part over the entire fruit, and ultimately passes into putrefaction.

Diastase, or gluten of barley altered by germination, brings a solution of sugar, and also gelatinous starch, not into vinous, but into lactic acid fermentation, whereby the sugar is converted, without any evolution of gas, into lactic acid and a small quantity of acetic acid; towards the end of the fermentation, part of the dissolved diastase is precipitated in a further state of alteration, as wine-ferment, which then brings the rest of the sugar into the state of vinous fermentation.

Fresh animal membranes, such as bladder and the lining membrane of the stomach, immersed in water in an open vessel, pass through certain successive stages of decomposition, and accordingly, in the first phase of their decomposition, bring a solution of sugar into the state of lactic acid fermentation, in the second, into mucous fermentation, and in the third, into vinous fermentation.

Moist casein exposed to the air for a short time, and the curdled emulsion produced by the acidification of almond-milk, bring a solution of sugar into the state of lactic acid fermentation; but the lactic acid thereby produced combines with the ferment, and stops its action, unless it be neutralized with an alkaline carbonate. (Bouton & Frémy.)—By the further action of the ferment, the lactic acid formed in the earlier stage of the operation is converted into butyric acid, with evolution of carbonic acid and hydrogen gases. (Pelouze & Gélis.)—Between 24° and 30°, casein acquires the properties of wine-ferment. (Liebig.)

Mucous fermentation appears to be most readily induced when the solution is very dilute, and the wine-ferment is either not fully developed, or has been brought by the action of various substances, a trace of sulphuric acid, for example, into a less efficient state. Thus, according to Desfosses, the filtered decoction of beer-yeast brings a solution of sugar at 30° into the state of mucous fermentation.

The juice of mangel-wurzel, turnips, or onions, which contains common sugar and a nitrogenous substance, passes at ordinary temperatures into vinous fermentation, yielding carbonic acid, alcohol, and yeast; but between 30° and 45°, it gives off but a small quantity of gas, and accordingly forms but little alcohol, the sugar contained in it being for the most part converted into grape-sugar, and afterwards into lactic acid, mannite, and mucilaginous matter. (Liebig.)

The fermentation of protein- and gelatin-compounds is prevented by a variety of circumstances, which likewise interrupt its further progress if it has already begun. The same circumstances likewise prevent or interrupt the fermentation of any fermentable materials that may be mixed with the ferment.

Among these circumstances are the following:

1. *Exclusion of the air.*—Keeping the substances in vacuo, in water free from air, in hydrogen, nitrogen, carbonic acid, and other gases, which cannot furnish oxygen to the nitrogenous substances; covering them with oil, butter, tallow, wax, or resin.—Wood immersed in the depths of lakes and peat-mosses, where no oxygen absorbed from the air

can reach it, because it is intercepted on the way by organic substances diffused through the water, remains unaltered for thousands of years.—This exclusion of air may prevent incipient fermentation, but does not usually interrupt the progress of that which has already begun. According to Schwann (*vid. inf.*), exclusion of air acts, not by intercepting oxygen, but by preventing the admission of the germs of microscopic plants and animals diffused through the air (*vid. inf.*).

2. *Dryness.*—Perfect dryness prevents every kind of fermentation, and seldom allows even of slow combustion: *e. g.*, the preservation of wood for three thousand years in Egyptian tombs, where it has been exposed only to the action of tolerably dry air.

3. *Freezing temperature.*—Water in the solid state is quite inactive, and does not allow fermentation to go on; but even at a few degrees above 0°, certain kinds of fermentation do not take place, and others are very slowly produced. All kinds of fermentation appear to take place most readily between 20° and 40°.—Mammoths have remained undecomposed for thousands of years in the ice of Siberia.

4. *Boiling Heat* prevents incipient fermentation, and completely stops that which has already begun, either because all ferments are altered by it, in a similar manner to albumen, which, when boiled hard, is scarcely susceptible of putrefaction; or because it kills the microscopic plants and animals and their germs; or from both causes together. Fermentation prevented or interrupted by a boiling heat, does not recommence after cooling, if the air be perfectly excluded, because either oxygen or living germs are required to produce new ferment.

On this principle is founded Appert's process, by which easily decomposible articles of food and drink, such as meat, fish, vegetables, milk, &c., may be preserved for years,—viz., by packing them in air-tight bottles or soldered tin-cases, heating the vessels for several hours in boiling water, and keeping them carefully closed. To explain this action, we may either suppose, with Liebig, that the small quantity of oxygen contained in the enclosed air is taken up by the organic matter, without being able to produce ferment at that temperature, or, with Schwann, that the microscopic organisms are killed by the heat.

If the air be admitted, the boiled substance passes again, after a while, into the fermenting state.—If, however, grape-juice, milk, meat, &c., be exposed once a-day to a boiling heat, without being protected from the air, and the small quantity of reproduced ferment thereby rendered inactive, before it has time to act upon the rest of the mass, fermentation may be prevented for any length of time.

5. *Antiputrescent* or *Antiseptic Substances.*—By the addition of various substances, organic and inorganic, fermentable bodies are deprived of their tendency to fermentation, and fermentation already commenced is interrupted.

These antiputrescent bodies probably act in various ways:

a. They abstract water from the fermentable substance.

b. They form with it a compound less liable to fermentation.

c. They decompose the ferment in such a manner as to deprive it of its tendency to fermentation.

d. They take from the surrounding air, and also from the ferment already oxidised by it, the oxygen required for fermentation.

e. They probably kill the fungi and infusoria and their germs.

The action mentioned in *a* is probably exerted by powdered sugar in contact with meat and fresh cut-up vegetables; the solution of sugar

thereby formed is too strong to ferment.—*a* and *b* together: Alcohol and wood-spirit; common salt, nitre, &c.—*b*: The stronger mineral acids, such as sulphuric acid, alum, ferric sulphate, corrosive sublimate, and other heavy metallic salts; tannin, creosote.—*c*: Chlorine, hyponitric acid, and chromate of potash.—*d*: Probably, sulphurous acid.—*e*. Arsenious acid, as also corrosive sublimate, and several other of the substances above mentioned. Arsenious acid and corrosive sublimate kill fungi and infusoria; *Nux vomica*, only the latter.

Phenomena exhibited by certain vegetable and animal substances during fermentation.

Wood.—Wood-shavings moistened with water and enclosed in a space containing air, convert the oxygen of the air into an equal volume of carbonic acid gas, but at the same time produce from their own oxygen a large quantity of water, so that the brown mould-like substance, into which the wood is converted by this process—which consists of decay and putrefaction together—contains a larger per-centage of carbon than the wood. (Saussure.) When the air is excluded, moist wood-shavings likewise give off a small quantity of carbonic acid gas, and are converted into a pale, rotten substance, containing a smaller per-centage of carbon than the wood. (Saussure.)—Wood in this altered state possesses the property of shining by slow combustion after exposure for some time to the air. (I., 191.)—Wood which putrefies under water, emits carbonic acid and marsh-gas, together with a small quantity of nitrogen. (W. Henry.) [For further details, *vid. Preservation of Wood*; also *Woody Fibre.*]

Seeds and Soft Parts of Plants.—Four peas, weighing 1 gramme, macerated in 4 grm. of water over mercury, till they begin to give off gas—during which time they take up 1 grm. of water—then introduced into 200 cub. cent. of different gases together with various quantities of water over mercury, and left there in the shade, exhibit the following results: 1. In oxygen gas, under 6 grm. water, for 8 days at 18°: they absorbed 72·2 cub. cent. oxygen gas; evolved 61·0 carbonic acid and 1·6 hydrogen.—2. Other softened peas in oxygen gas without water, absorbed 45·0 cub. cent. oxygen; evolved 39·0 carbonic acid, but no hydrogen.—3. Other peas under 1 grm. of water at 23° for 3 days, absorbed 1·2 cub. cent. oxygen, evolved 2·3 nitrogen, 5·9 hydrogen, and 14·7 carbonic acid.—4. Other macerated peas kept in air, without water, for 48 hours, absorbed 10·7 cub. cent. oxygen and 1·4 nitrogen, and evolved 13·2 carbonic acid.—5. The peas of 3, afterwards introduced into fresh air [for 48 hours?], absorbed 11·25 cub. cent. oxygen gas and 1·4 nitrogen, and evolved 16·7 carbonic acid.—6. Other macerated peas also left in air for 4 days, absorbed 17·4 cub. cent. oxygen gas and 1·0 nitrogen; evolved 17·4 carbonic acid.—7. Four peas undergoing slow putrefaction in 200 cub. cent. of nitrogen gas, absorb in 8 days, 3 cub. cent. nitrogen, and evolve 2·5 carbonic acid; but in a state of rapid putrefaction, they absorb no nitrogen in 8 days, but give off from 30 to 35 cub. cent. carbonic acid.—8. In a mixture of 100 cub. cent. nitrogen gas and 100 cub. cent. hydrogen, 4 peas macerated as above, absorb 2·7 cub. cent. nitrogen gas and 2·6 hydrogen, and evolve 12·5 carbonic acid.—9. During slow putrefaction in hydrogen gas, peas absorb little or none of that gas, but evolve a small quantity of carbonic acid.—10. In a mixture of equal measures

of hydrogen and carbonic acid gases, they do not absorb any of the former. (Saussure.)

Young leafy stems of *Medicago sativa* (corresponding to 0·8 grm. of the dried plant), brought under water to a state of commencing putrefaction, and then suspended for 48 hours in 268 cub. cent. of air at 19°, absorbed 23·7 cub. cent. oxygen gas, scarcely 1·8 nitrogen, and evolved 20·7 carbonic acid gas. Another sample of lucern brought under water to a state of fermentation, then beaten to a pulp, wrapped up in gauze, and suspended for 8 days in 200 cub. cent. nitrogen gas, absorbed at 17°, 4·8 cub. cent. nitrogen gas and an equal quantity of carbonic acid, without any hydrogen. (Saussure.)

In other cases, on the contrary, nitrogen gas is evolved during putrefaction, especially in the latter stage. Four peas macerated as above till gas begins to go off, evolve no nitrogen, when immersed in pure carbonic acid gas, which stops the putrefaction; but in a mixture of carbonic acid and nitrogen, they evolve 7·7 cub. cent. nitrogen, 3·8 hydrogen, and 18·0 carbonic acid.—Four peas macerated for only one day, and immersed in a mixture of 100 cub. cent. carbonic acid and 100 nitrogen at 19°, evolve in 8 days, 1·75 nitrogen gas, 1·3 hydrogen, and 24·1 carbonic acid; but 4 peas, previously macerated for 6 days, evolve 4·0 cub. cent. nitrogen, 2·7 hydrogen, and 4·0 carbonic acid. Peas macerated for 6 days, and in a state of active putrefaction, may give off nitrogen, together with carbonic acid and a certain quantity of hydrogen, even when placed in an atmosphere of pure nitrogen (and though the carbonic acid, as it escapes, may be removed by potash), but less than they would evolve in nitrogen gas mixed with an equal quantity of carbonic acid; *e. g.*, in presence of potash, 1·8 cub. cent. nitrogen and 3·2 hydrogen in 8 days. (Saussure.)

When peas, lentils, French beans, colza, wheat or barley, are kept for two months in the summer, under a fourfold weight of water free from air, in a tube over mercury, and standing in the shade, no nitrogen gas is evolved, but carbonic acid mixed with hydrogen, or, as in the case of rye and barley, merely carbonic acid gas (but these also yield hydrogen gas, if there be any air above the water). The hydrogen is evolved more abundantly as the temperature is higher, and the putrefaction is further advanced. Three grammes of peas evolve in two months 342 cub. cent. of a mixture of gases containing 98 parts of hydrogen. Three grammes of lentils yield 64 cub. cent. of a gaseous mixture, 7 of which are hydrogen; if they ferment between 12° and 15°, they yield nothing but carbonic acid. Three grammes of wheat yield only 38 cub. cent. of mixed gases; barley still less. The hydrogen gas given off by peas contains a small quantity of marsh-gas or carbonic oxide, and hence, when exploded, yields 2·64 p. c. carbonic acid gas. (Saussure.)

It appears then that peas in a state of slow putrefaction absorb nitrogen gas, if they are placed in an atmosphere of nitrogen, common air, or nitrogen mixed with hydrogen; an excess of oxygen interferes with the absorption of the nitrogen. In a state of rapid putrefaction, they give off nitrogen in a mixture of nitrogen and carbonic acid; a smaller quantity in pure nitrogen gas; and none in hydrogen or carbonic acid, these last-mentioned gases putting too great a check on the putrefaction. (Th. Saussure, *Bibl. univ.* 56, 130; also *J. pr. Chem.* 3, 160); *comp.* also Th. Saussure (*Ann. Chim. Phys.* 11, 398).

Wheat left to itself in a flask containing air and provided with a gas-delivery tube, gives off carbonic acid and hydrogen gas, first in the ratio

by volume of 3 : 2, then of 2 : 1, and lastly of 3 : 1; the hydrogen evolved is free from carbon. The residual watery liquid contains butyric acid. If in this experiment the air be completely excluded by removing it as far as possible from the beans after their immersion in water, by repeated pumping, the fermentation which takes place is very imperfect, and yields but very little gas, containing 3 vol. carbonic acid to 2 vol. hydrogen. White beans treated like the wheat in the first experiment first give off pure carbonic acid gas and then a mixture of 2 vol. carbonic acid to 1 vol. hydrogen, the latter being free from carbon. At the end of 9 weeks, the evolution of gas is finished, and the residual liquid contains large quantities of ammonia and butyric acid.—Peas give off carbonic acid at first, then a mixture of that gas with hydrogen and traces of sulphuretted hydrogen, at the same time producing butyric acid.—Grains of maize give off in 8 weeks but very little carbonic acid, but no hydrogen, and yield but a trace of butyric acid, the formation of which is intimately connected with the evolution of hydrogen. (Erdmann & Marchand, *J. pr. Chem.* 29, 465.)

Milk.—Two glass bottles, each containing 3 ounces of water, were three parts filled with fresh milk, then well closed with ground stoppers, and heated for two hours in boiling water. The air of one of those bottles, examined eudiometrically after boiling, still contained 16·7 p. c. of oxygen gas. The second bottle was kept under water for 19 days in June, at a temperature between 20° and 25°, and then opened, that the milk might be examined; no escape of gas took place when it was opened. The milk was not curdled, did not redden litmus, and had the taste of sweet fresh milk. On subsequent exposure to the air for a few days, it curdled and acquired the power of reddening litmus.

The same experiment was repeated with four other bottles, the first being filled with milk to $\frac{5}{6}$ of its bulk, the second to $\frac{2}{3}$, the third to $\frac{1}{2}$, and the fourth only to $\frac{1}{4}$. After two hours' heating in boiling water, the air of the first bottle still exhibited a proportion of oxygen amounting to 16·4 per cent. The other bottles were kept under water for six weeks in July and August. The milk remained fluid: but on opening these three bottles a mixture of gases issued with great violence; this gas was collected from the third and fourth bottles, and found to contain a large quantity of carbonic acid, but neither oxygen nor hydrogen. The milk of the fourth bottle still remained liquid, but reddened litmus, and had not a putrid but a spirituous odour. In fact, when distilled in the apparatus described in *Pogg.* 42, 559, it yielded a few drops of an inflammable distillate which smelt like alcohol. The milk curdled during distillation, and was afterwards found to be still strongly acid; a proof that carbonic acid was not the only acid produced. (Th. v. Dusch & Gm.)

Hence we may conclude that when milk is boiled for two hours with a small quantity of air, only the smaller portion of the oxygen is absorbed, and yet the oxygen which remains causes no fermentation; but if the quantity of milk be smaller in proportion to that of the air, carbonic acid, lactic acid, and alcohol are produced, even if all further access of air be prevented. The former fact does not agree with the theory of Liebig, nor the latter with that of Schwann.

Blood and the more solid parts of Animals.—Freshly drawn blood placed, together with air, over mercury at ordinary temperatures, does not act upon the air in the first 12 hours; subsequently the quantity of

gas diminishes, because the carbonic acid gas formed from the oxygen is absorbed; but when the blood becomes saturated with carbonic acid, ammoniacal putrefaction takes place, and the volume of gas increases in consequence of the evolution of carbonic acid. Fibrin of blood similarly treated, converts all the oxygen of the air in 24 hours into carbonic acid, a small portion of which is absorbed by the decomposed mass; afterwards, the volume of gas continually increases, in consequence of the evolution of carbonic acid. (J. Davy.)

Of the more solid parts of animals, those which putrefy most quickly in the fresh state are the brain, muscles, spleen, liver, and other glands; they give off carbonic acid, even in the first few hours, and increase the volume of gas in 24 hours; then follow, the skin, periosteum, dura mater, intestines, veins, arteries, and stomach, which produce carbonic acid in 24 hours, and increase the volume of gas in an interval varying from 48 to 72 hours. Putrefaction takes place still more slowly in tendons, intervertebral substance, cartilage, and bones. (J. Davy.)

When putrefaction has once commenced, it goes on even after the oxygen has been completely absorbed, carbonic acid and ammonia being disengaged, and sometimes also a small quantity of sulphuretted hydrogen or (especially in the case of muscles), of marsh-gas. (J. Davy.)

During this putrefaction heat is evolved, and in the case of the more quickly putrefying animal matters, such as blood, fibrin, the heart and other muscles, the liver, dura mater, tendons, &c., the temperature rises from 1° to 6°. In slowly putrefying substances, the evolution of heat is not perceptible, in consequence of the slowness of the action, but it undoubtedly takes place. Animal substances are converted by putrefaction—with formation of carbonic acid and ammonia—into a semifluid mass, which serves as food for the larvæ of flies, and is gradually resolved into ammonia and extractive matter. Putrefaction takes place more quickly under diminished pressure in a tube standing over mercury than under the ordinary atmospheric pressure, because the products of putrefaction, viz., carbonic acid and carbonate of ammonia, exert an antiputrescent action. Thus a piece of muscle immersed in a solution of 3 grains of carbonate of ammonia in an ounce of water, does not putrefy for 4 weeks; and a piece of *jejunum* remains unchanged for 8 months in a solution of 5 grains of carbonate of ammonia in an ounce of water. (J. Davy, *Edinb. Med. and Surg. J.* No. 105, 243.)

Casein, or gluten, immersed in water, gives off a stinking mixture of carbonic acid and hydrogen gas; imparts to the water, first free acid, together with sulphuretted hydrogen, afterwards carbonate of ammonia; and is converted into oxide of casein. (Proust.)

A solution of gelatin passes at once into the state of ammoniacal putrefaction, without previously going through the acid stage.

In dilute aqueous solutions of substances which are inclined to putrefy, innumerable infusoria are quickly formed.

The phosphorescence of putrefying fish (I., 189), and the light of the ignis fatuus, perhaps arise from phosphuretted hydrogen gas evolved in putrefaction.

Muscular flesh keeps tolerably well at a few degrees above 0°, but at 15° it passes into slow, and at 25° into rapid putrefaction. It then becomes softer, yields a watery liquid, gives off an almost intolerable ammoniacal odour, which gradually diminishes, and at length ceases altogether; and is converted first into a thin pap, and afterwards into a nearly inodorous, brown, fusible mass (mould), which weighs but very

little. (Fourcroy, *Syst. des Connaiss. Chim.* 2, 96; *comp.* Priestley, *Exp. and Observ. on different kinds of air*, 1, 70, and 123; 3, 340. Pringle, *Phil. Trans.* 46, 480; Crell, *Crell, chem. J.* 1, 158.) The greenish colour of meat, at the commencement of putrefaction, is perhaps due to the presence of sulphide of iron. (Gm.)

When a piece of muscular flesh is left to itself [on what support?], a second piece laid upon a zinc plate, and a third on a plate of copper, the first piece begins to putrefy on the following day, but the other two not till after a longer time, and with formation of different products; for the piece laid upon the zinc gives off ammonia and carburetted hydrogen [?], while that upon the copper yields a large quantity of acid, which forms acetate of copper. Corresponding differences are exhibited by the different parts of a piece of flesh placed in the circuit of the galvanic battery. (Matteucci, *Ann. Chim. Phys.* 42, 310; also *Schw.* 58, 369; also *Br. Arch.* 36, 329).

Fresh beef, enclosed in oxygen gas, exhibits for the first few days a finer red colour than before, but afterwards becomes paler and moist, exudes transparent drops, which afterwards turn milky, and becomes putrid in 11 days; if left for 51 days, it deliquesces and emits an insupportable odour. A great part of the oxygen gas is found to be converted into carbonic acid.—In *Hydrogen gas*, meat acquires a light brown colour; becomes somewhat drier and more solid, and after 11 days is not at all putrid, but has a scarcely perceptible sour smell; if afterwards exposed to the air, it dries up to a hard mass without putrefying. In another experiment, the meat, even after 54 days, exhibited the appearance of fresh meat, but stank horribly, though its odour was different from that of meat putrefied in oxygen gas; the hydrogen was afterwards found to be mixed with carbonic acid.—In *Carbonic acid gas*, meat appears brown or red at first, but afterwards becomes paler. After 11 days, it resembles boiled meat in colour, and is very soft, but not sticky; its odour is very faintly acid, and on exposure to the air it does not putrefy, but dries up. After 51 days' immersion in carbonic acid gas, it exhibits the colour and consistence of boiled meat, and is not at all putrid.—In *Sulphurous acid gas*, meat immediately loses its colour; after 76 days, it becomes much harder and drier than fresh meat, smells of sulphurous acid, and on exposure to the air dries up in four days without putrefying.—*In gaseous Fluoride of Silicium*, meat exhibits nearly the same characters.—In *Nitric oxide gas*, it immediately acquires a brighter red colour, and if taken out after 11 days, exhibits a fine red colour, is nearly inodorous, acquires a dark colour on exposure to the air, and dries up quickly. A piece of meat left in this gas for 134 days, appears bright red and solid, and smells somewhat of nitric acid.—In *Ammoniacal gas*, meat acquires a brighter red colour, which it retains if kept in the gas for 76 days. When taken out, it is soft, inodorous, and does not putrefy on exposure to the air, but dries up to a brown, shining mass. (Hildebrandt, *N. Gehl.* 7, 283; 8, 180; *Schw.* 1, 358).

Similar experiments were formerly made by Priestley (*Exp. and Observ. on diff. kinds of air*, 1, 123); by Brugnatelli (*Crell, Chem. Ann.* 1787, 2, 483); and more especially by Böckmann (*Scher. J.* 9, 240).

If a bottle, containing water with meat, be well boiled, and, while the open air is excluded, only air be passed through it, which has been previously transmitted through a red-hot glass tube, no putrefaction or formation of infusoria takes place even in several weeks; but on opening the bottle, these phenomena soon show themselves. Hence it is probable

that the air contains germs of infusoria, which are destroyed by ignition; but the germs contained in the unignited air pass into the organic matter, developing themselves and increasing at its expense, and the organic substance is thereby brought into the state of putrefactive decomposition. Arsenious acid and corrosive sublimate, which exert a poisonous action both on infusoria and on fungi, prevent putrefaction; but extract of *nux vomica*, which is a strong poison for infusoria, but not for fungi, stops those putrefactive changes which accompany the formation of infusoria, such as the evolution of sulphuretted hydrogen, but allows mouldy putrefaction to go on. Perfectly similar phenomena are exhibited in vinous fermentation (*q. v.*). (Schwann, *Pogg.* 41, 184.)

This experiment was repeated with the same result, both with meat and broth, by Ure. (*J. pr. Chem.* 19, 186.)

Helmholtz (*J. pr. Chem.* 31, 429) proceeded with similar experiments, as follows. The flask containing the organic matter is closed with a well-sealed cork, through which pass two glass tubes *a* and *b*, bent at right angles. The outer end of the conducting tube *a* is drawn out to a point, and that of the tube *b*, which serves as a sucking tube, is bent downwards. The liquid in the flask is boiled till vapour issues from the outer ends of both tubes; the tube *a* is then closed with sealing-wax, and part of the tube *b* is kept at a red heat by a spirit-flame, in order to heat the air, which flows into the tube as it cools, the heat being gradually extended to the outer end, whereupon this end is also closed with sealing-wax. The air which has entered the flask soon gives up the greater part of its oxygen to the organic substance. To allow a change of air to take place, each of the tubes is then heated to redness at one point, the ends are opened, and air drawn out from time to time at the end of *b*, which causes fresh air to enter the flask through the tube *a*. In this manner parts of animals, or pieces of meat, may be kept unaltered for 8 weeks in hot summer weather, in contact with water, solution of gelatin, or grape-juice, without alteration of appearance, taste, smell, or behaviour with re-agents. But as soon as any portion of unignited air is admitted, or if the vessel be not perfectly closed, putrefaction or fermentation takes place in 2 or 4 days; with a solution of gelatin, the change may be recognised, before the liquid begins to smell, by the decoloration of tincture of litmus mixed with it. Urine, on the contrary, enclosed in a sealed glass tube, and heated in water to 100°, exhibits the same slow decomposition into carbonate of ammonia as in the air, but without any appearance of putrefactive fermentation. Hydrocyanic acid likewise decomposes when heated to 100° in a sealed tube, as quickly as when the air has free access to it. ¶ Döpping & Struve (*J. pr. Chem.* 41, 255; *Jahresber.* 1847–8. 472), in repeating these experiments, obtained different results, and came to the conclusion that all nitrogenous organic bodies suffer decomposition, even under the influence of air which has been exposed to a red heat, and that the phenomena, in the preceding experiments, are merely retarded and altered by the influence of the boiling heat. ¶

If a wide test-tube be completely filled with a fermentable material, then bound round with bladder, heated in boiling water, and immersed with the bladder downwards, in a putrefying or fermenting liquid of the same kind, the following effects are produced: Grape-juice in the tube, surrounded with fermenting *must* (new wine in a state of fermentation), remains unaltered, excepting that it acquires by endosmose a vinous taste and smell; a similar result was formerly obtained by Mitscherlich

(*vid. Vinous fermentation*).—Meat with water in the tube putrefies almost as quickly as in the open air. But instead of deliquescing as it usually does, and forming a turbid, semifluid mass, it retains its structure, becomes more solid than boiled white of egg, and, when examined by the microscope, exhibits neither infusoria nor plants. Solution of gelatin also putrefies under these circumstances as quickly as in the air, but without turbidity. It appears then that meat and gelatin may be brought into a state of putrefaction by dissolved putrefying substances which can pass through the bladder; the presence of infusoria is unnecessary, but at the same time, no infusoria are produced during the putrefaction; in the case of must, on the contrary, the presence of fermentation-fungi is essential. Thus far Helmholtz.—Löwig suggests that the outer putrefying liquid may have merely penetrated by endosmose into the bladder, and undergone further decomposition, without bringing the matter originally enclosed in the tube into the putrefying state, inasmuch as the meat preserved its structure unaltered.

Urine.—Urea remains unaltered when dissolved in pure water; but in the urine, in which it exists in the state of aqueous solution together with mucus and other substances, it changes with various degrees of rapidity into carbonate of ammonia:

$$C^2H^4N^2O^2 + 2HO = 2(NH^3,CO^2).$$

The decomposition is accelerated by the presence of certain substances, and, according to Jaquemart (*N. Ann. Chim. Phys.* 7, 149; also *J. pr. Chem.* 29, 188), in the following manner: Healthy urine, in a perfectly clean vessel, decomposes very slowly, even at 32° C. and during storms; it is not till the ninth or tenth day that a sufficient quantity of carbonate of ammonia is formed in it to effervesce with acids; on the fourteenth day it gives off, on the addition of dilute sulphuric acid, 9 times its volume of gas, $\frac{4}{5}$ of which consist of carbonic acid, a quantity which can only have been produced by the decomposition of all the urea contained in the urine. (It is here understood, that the mixture of urine and sulphuric acid retains its own volume of carbonic acid in solution, and this quantity is added to the carbonic acid actually evolved.) Urine mixed with 1 per cent. of beer-yeast, gives with acids 6·7 volumes of gas on the fifth day, and 12·6 vol. on the seventh. With 4 per cent. of beer-yeast it gives 10·4 vol. on the fifth day, and 12·6 vol. on the seventh. Mixed with 2·5 per cent. of glue, it gives 6·7 vol. on the second day, and 10 vol. on the third. Mixed with a small quantity of carbonate of ammonia, it yields 6·3 vol. carbonic acid on the fourth day (after deduction of that which proceeds from the carbonate of ammonia added), and on the fifth day the decomposition is complete. Hence fresh urine mixed with 8 per cent. of putrefied urine, yields 6 vol. of gas on the second day, and is completely decomposed on the third. Urine collected in receptacles in public places, passes quickly into ammoniacal putrefaction. On emptying these receptacles, washing them superficially without removing the deposit on their sides and bottom, then introducing fresh urine for only 20 minutes, and filtering it, this urine decomposes completely in 24 hours; if it be mixed immediately after filtration with another portion of fresh urine, the mixture becomes very turbid on the first day, gives off 6 vol. carbonic acid gas in 24 hours, and is completely fermented by the fourth day. The white deposit produced in public receptacles of urine during fermentation, exhibits very strong decomposing power;

when collected on a filter, dried between paper, and mixed with 50 times its weight of fresh urine, it produces rapid fermentation, which sometimes terminates in 24 hours.

¶ According to C. Schmidt (*Ann. Pharm.* 61, 168), urea mixed with yeast is quickly resolved into carbonic acid and ammonia. When mixed with yeast and a small quantity of sugar, it does not decompose till the sugar is completely fermented. With a certain proportion between sugar and yeast, a kind of equilibrium is established; with a larger quantity of sugar, the urea is protected from decomposition; and with a smaller quantity of sugar, the urea is decomposed with greater or less rapidity, according to the excess of yeast present. A given quantity of yeast decomposes only a definite quantity of urea; equal quantities of yeast and water mixed with different quantities of urea always yielded the same amount of urea in a given time. Fungi are not essential to the fermentation of urea. A solution of glue mixed with urea, phosphate of soda, and sulphate of magnesia, which had been filtered, heated to the boiling point for half an hour, and then exposed to a current of air previously passed through sulphuric acid, yielded, after 8 days, a quantity of phosphate of magnesia and ammonia, equal to that which the same liquid would have given under similar circumstances if exposed to to the air in its ordinary state. ¶

Putrefaction of Cowdung.—When dung, rendered loose by mixture with chopped straw, is floated on water in a basin, and covered with an inverted bell-jar, it converts the oxygen of the air into a nearly equal volume of carbonic acid gas, imparts nitric acid to the water in the course of a few days, and likewise nitrate of ammonia if the air be not renewed, because, in this case, hydrogen is also evolved. If the cowdung be well covered up with clay, it likwise absorbs oxygen abundantly; gives off carbonic acid, but no hydrogen; rises in temperature by 12°—15°; and acquires first a pungent ammoniacal and afterwards a musty smell, at the same time diminishing considerably in quantity, and being converted into a dry, light, porous, black mass, which bears a strong resemblance to peat, and decays very slowly. No nitric acid is found in the water surrounding the bottom of the jar. (Thaer & Einhof, *A. Gehl.* 3, 290.)

Theories of Fermentation.

1. In vinous fermentation, the nitrogenous matter of the liquid takes up oxygen, and is converted into a ferment, and this ferment, by its catalytic power (I., 114, 115), causes the sugar to resolve itself into carbonic acid and alcohol. (Berzelius.) This is to give a name to the fact, not to explain it.

2. The nitrogenous body, by contact with the oxygen of the air, undergoes a change of composition; the equilibrium of the attractive forces which held its particles together is thereby disturbed; new compounds are formed; and the body undergoes progressive transformations, which, now that the equilibrium of the forces is destroyed, go on, even if further access of air be prevented. The alteration of arrangement in the atoms of the elements produces a motion in the compound atom of the nitrogenous body, which motion is transferred from one compound atom to the next; and in this manner the decom-

position or fermentation is propagated throughout the whole of the nitrogenous body.

Now, when a nitrogenous substance in this state of decomposition comes in contact with another substance, such as sugar, which would not ferment by itself, the motion by which the elementary atoms of the former body are affected, is also transferred to the contiguous atoms of the latter, causing the elementary atoms contained in the compound atoms of the latter to assume new arrangements and enter into new combinations: and in this manner the latter substance is made to resolve itself into new products. (Liebig.)

This mode of explanation is likewise unsatisfactory. Admitting for a moment that the oxygen brings the nitrogenous matter into a state of progressive decomposition, and thereby causes a motion of the elementary atoms which form the compound atom of that substance, still we cannot suppose that this atomic motion extends beyond the sphere of the atom of the ferment into that of a neighbouring atom of sugar. For, the cause of this atomic motion is the tendency of the elementary atoms contained in an atom of the ferment, to unite *among themselves* in new proportions; there is no cause assigned to induce them to move out of their sphere. But even supposing that the motion of the elementary atoms in the ferment should go so far as to cause one of them to impinge upon an elementary atom of the sugar-atom, and endeavour to push it out of its place, such impact would probably cause a change of place, not merely in the individual elementary atom of the sugar which was struck, but in the compound atom as a whole. If, indeed, we suppose that this mechanical impact of one atom upon another is capable of altering the state of combination in the sugar-atom, it is not very easy to see why the agitation of sugar-water with sand or small shot, by which some of the elementary atoms of the sugar must receive a stronger impulse than others, should not also produce a decomposition of the sugar. Neither is it easy to understand why other changes which take place in the sugar-solution,—even when they are accompanied, as in the case of the ferment, with evolution of gas,—*e. g.*, the action of acids on a solution of sugar and carbonate of potash, or the solution of zinc in a sugar-solution mixed with acid—do not produce decomposition of the sugar;—why it is only a particular kind of matter in a peculiar state of decomposition, which, by the motion of its atoms, can induce fermentation; why this substance, in its various stages of decomposition, brings the sugar into totally different states of fermentation; and why—since, according to Liebig, the soluble portion of the yeast, which can penetrate the bladder, is the more active portion—a sugar-solution separated from the yeast by a bladder, is found, as in the experiments of Mitscherlich and Helmholtz, not to enter into fermentation. ¶ Döpping & Struve (*J. pr. Chem.* 41, 255), in repeating Helmholtz's experiments, sometimes observed a slight evolution of gas in the sugar-solution in the tube, so long as the outer solution was in the fermenting state; subsequently also they found yeast-cells in the former solution; in several other experiments, however, this effect was not observed. ¶

Moreover, the experiments of Schwann & Helmholtz (p. 106) which show that air which has been previously passed through a red-hot tube, and is thereby freed from the germs of microscopic organisms, does not induce fermentation or putrefaction in nitrogenous bodies, throws great doubt on the fundamental proposition that oxygen alone is sufficient to bring the nitrogenous matter into the state of ferment. ¶ But on this

point also the experiments of Döpping & Struve give results different from those of Helmholtz (*comp.* p. 106). ¶

3. According to Schwann, the air contains the germs of microscopic plants and animals; and when these germs find a fitting soil, such as is offered by various nitrogenous bodies, they develop themselves therein, producing fungi and infusoria, which then, in a manner not yet explained, induce the fermentation of sugar, &c. In vinous fermentation, Mitscherlich supposes that the yeast-fungi act like contact-substances (*vid. Vinous Fermentation*).

¶ Blondeau (*N. J. Pharm.* 12, 244 and 336) also maintains that fermentation in all its forms depends on the development of fungi. Alcoholic fermentation he attributes to a fungus which he calls *Torvula cerevisiæ;* lactic acid fermentation to *Penicillium glaucum.* The latter fermentation takes place after the former, when a mixture of 30 grammes of sugar and 10 grm. yeast with 200 cub. cent. water at the temperature of about 25°, is left to itself for some time, after the termination of the vinous fermentation (which is completed in about 2 days). Beer-yeast mixed with a little water and left to itself in a dark moist place, was found to contain germs of *Torvula cerevisiæ* and *Penicillium glaucum;* when the liquid was filtered, the former of these remained on the filter and brought a solution of sugar into the state of vinous fermentation; but the latter being extremely small, ran through the filter, and the filtrate brought sugar-water into the state of lactic acid fermentation. *Acetic acid* fermentation depends on the development of *Torvula aceti.* The conversion of nitrogenous substances into fat (*e. g.*, of casein in the preparation of Roquefort cheese, and of fibrin under similar circumstances), which Blondeau distinguishes by the term *fatty* or *adipic Fermentation* (*fermentation adipeuse*), is produced by *Penicillium glaucum* or *Torvula viridis;* and in butyric acid fermentation, and urinous fermentation (the conversion of urea into carbonate of ammonia), the action depends on the development of *Penicillium glaucum.* (Blondeau.) ¶

Against this view Liebig raises the following objections:

Beer-yeast, which is supposed by Schwann, Turpin, and others, to consist of fungi, does not possess the composition of true fungi, but of gluten.—It has never yet been specified in what manner these microscopic organisms effect the decomposition of fermentable substances. Are the products of fermentation and putrefaction the excrements of these living beings, to which the fermentable substance serves as food? Or do these organisms transform the original fermentable substance into new compounds (products of fermentation) by an external exertion of their vital force?—If vinous fermentation were a consequence of the more perfect development of fungi—as we might, perhaps, suppose to be the case in the fermentation of beer and wine—beer-yeast ought not to bring sugar-water into a state of fermentation, inasmuch as the sugar-water contains no nitrogenous matter which can serve as food to the fungi composing the yeast, but on the contrary these fungi disappear during the fermentation.—Sugar-water is likewise brought into the state of vinous fermentation by contact with cheese or almond-milk, though in this case no fungoid bodies are developed like those of the vinous ferment, as in the preparation of beer, or the fermentation of grape juice.—In thousands of cases, no infusoria can be detected in putrefying cheese, blood, urine, or bile, or they do not make their appearance till the putrefaction has gone on for some time; hence they cannot be the cause

of the putrefaction, but are merely developed from germs existing in the air, because these germs find nourishment in the putrefying substance. It is true that they then accelerate the decomposition, because they feed upon the organic matter, and convert it by their vital action into carbonic acid, &c. When they have thus consumed all the nutriment, they die, and serve as food for infusoria of other species. All this may take place when the air has access to the putrefying substance; but bodies which putrefy out of contact of air, cowdung for example, never exhibit infusoria, which in fact would be killed by the sulphuretted hydrogen evolved. (Liebig.) ¶ Liebig also remarks (*Handwörterbuch der Chemie*, 3, 217), that in the fermentation of milk, when that liquid is left to itself for a while in vessels containing air and bound over with blotting paper, till fermentation and formation of lactic acid are completely established, not a trace of vegetable growth can be detected. He moreover observes that in the study of fermentation, attention has been too exclusively directed to the vinous fermentation, and conclusions of too great generality have been drawn from the phenomena observed in that particular process; whereas, the explanation of vinous fermentation ought rather to be deduced from the study of fermentation in the more general sense.

C. Schmidt (*Ann. Pharm.* 61, 168) is also of opinion that *fungi* are not the prime movers either in urinous (p. 108) or in vinous fermentation. He finds that the clear filtrate obtained by throwing almonds beaten up with water on a wetted filter, soon brings urea and grape-sugar into the fermenting state; and in the latter case, the fermentation may be in full play, although no trace of yeast-cells is discernible by the microscope, these cells not appearing till afterwards. If the saccharine liquid be left to itself for a week or a fortnight after the completion of the fermenting process, the groups of cells continue to grow in it, though no putrefaction takes place; the fungi, if washed and then introduced into a fresh solution of grape-sugar, grow in it vigorously, but excite but feeble and transient fermentation, if any; hence it appears that the growth of these plants is but a secondary phenomenon in fermentation. The loss of activity in bruised yeast depends, not upon the destruction of the fungi, but on the chemical change produced by the air during the long time required to bruise the yeast completely; the crushed yeast-cells convert sugar into lactic acid, with scarcely any evolution of gas.—Schmidt is also of opinion that [vinous] fermentation is, like etherification, a process in which one or more compounds, capable of splitting, at the very instant of their formation, into alcoholic and carbonic acid, are produced from one of the constituents of the yeast together with the elements of the grape-sugar,—just as sulphovinic acid is formed in the process of etherification. ¶

That fermentation and putrefaction do not actually depend upon the action of living beings, appears also from the observation of Helmholtz mentioned on page 106,—viz., that fresh meat separated from putrefying meat by a bladder, through which living organisms cannot pass, nevertheless passes into the state of putrefaction; the same conclusion is likewise supported by the second series of experiments with milk (p. 103). It must therefore be admitted, that, although living beings play an important part in some fermentations, the vinous, for example, and in others exert a marked influence on the course and products of the decomposition, still they cannot be regarded as the cause of the fermen-

tation; in fact, we do not as yet possess any perfectly satisfactory theor of these processes.

[For further details, see the several kinds of fermentation, especially *Vinous Fermentation*.]

Preservation of Organic Substances.

Preservation of Wood.

Wood consists principally of lignin or woody fibre; but in its cells there is deposited another substance insoluble in water and less disposed to putrefy, viz., the *incrusting matter of the wood*. The cells likewise contain the dried sap of the wood, consisting chiefly of sugar, gum, and albuminous matter. Wood felled at any time between the end of summer and the beginning of spring also contains starch, destined to supply the sap which rises from the roots in spring, with nourishment for the first leaves in the form of sugar. These substances, starch, gum, sugar (frequently also tannin), and more especially the albuminous matter, pass into the state of putrefaction, bring the woody fibre and incrusting matter into the same state, and favour the growth of fungi, as well as serving for food to the wood-worm. Morever, even pure woody fibre, such as linen, paper, &c., is liable to putrefy, though much less than wood in its natural state. According to Boucherie, oak-wood contains from 3 to 6 per cent. of matter soluble in water. Unwashed oak-shavings, kept moist with water for half a year, become mouldy and diminish considerably in weight; the same shavings, when washed, do not turn mouldy, and undergo scarcely any diminution in weight. (Boucherie.)

The preservation of wood intended to be exposed to air and water is effected, sometimes by removing the fermentable substances contained in it, sometimes by bringing these substances into a less fermentable state (partly by means of re-agents which likewise act as poisons on the wood-fungi), sometimes by impregnating and coating the wood with substances which oppose the access of air and water.

Removal of the constituents of the Sap.

Formerly, trees intended for ship-building were felled in winter; the ends of the branches cut off; and the trees suffered to lie with the bark on till the following summer, at which time they put forth buds and leaves, and thereby consumed the sap contained within them. Latterly, it has been the practice to fell the trees in spring, and work them up with the sap in them; in consequence of this, wood used for ship-building decays much more quickly now than formerly. (Carcy, *Dingl. Polyt. J.* 40, 215.)—In treating the trees by Boucherie's process (*vid. inf.*), the sap might be more completely removed by causing pure water to rise in the stem. Another method is to steep the wood as soon as it is felled, in water—best in a running stream—and keep it there for some months or a year. (Prechtl, *Polyt. Jahrb.* 3, 129.) According to Boucherie, the removal of the sap by this process is merely superficial. The wood may also be

enclosed in a box, and exposed to vapour of water under somewhat increased pressure. (Streicher, *Dingl. Polyt. J.* 36, 199.)

Diminution of the tendency to Putrefaction.

By exposing the wood to a strong heat; *e.g.*, the spiked ends of palings are often half-charred.—By saturating the wood with antiseptic liquids; *e.g.*, covering it with *Oil of Vitriol.* This liquid chars the wood externally, forms a compound with it, and prevents the attachment of cryptogamous plants. (*J. chim. méd.* 19, 668.)—Saturation of the wood with *Aqueous solutions of salts. Common salt:* Protects the wood from fungi, but is washed out by rain. (*Polyt. J.* 3, 449; 40, 216; 58, 479.) *Chloride of Calcium*, or the mother-liquor of many salt-springs containing that substance: Makes the wood very flexible, protects it from decay, by retaining a portion of its water, and thereby considerably diminishing its combustibility; but to protect it from putrefaction, a moderate quantity of crude acetate of iron must be added. (Boucherie.)—*Alum:* Less efficient as a protection from putrefaction than the salts of the heavy metals. (*Polyt. J.* 21, 286.)—*Green vitriol*, or its mother-liquid: Protects the wood from dry rot, but is in other respects not very efficient in preventing putrefaction. (Chapman; Strutzki, *J. pr. Chem.* 3, 188.)—*Crude acetate of Ferroso-ferric oxide*, obtained by dissolving iron turnings, smithy scales, &c., in pyroligneous acid. The antiputrescent power is partly due to the tar contained in this liquid. (Prechtl, Boucherie.)—*Blue vitriol.* Very efficient against dry rot and putrefaction.—*Protochloride of Copper.* Very efficient (*vid. inf.*). *Corrosive sublimate.* Very efficient. First recommended by Kyan (*Polyt. J.* 49, 456; 50, 299; 58, 486), whence the saturation of the wood with solution of corrosive sublimate is called *Kyanising.* According to Kyan, the best strength of solution is 1 pt. of sublimate in 60 of water. The sleepers on the Baden railway, which are steeped in a solution of 1 pt. corrosive sublimate in 75 parts water, have remained in excellent preservation for 7 years. Wood or cotton steeped in solution of corrosive sublimate does not give up a trace of mercury when immersed in water, but yields it to nitric acid; after being washed with water, it keeps quite as well as before. Hence corrosive sublimate forms an insoluble compound with woody fibre. Kyanized wood remains unaltered in a mould-pit for 5 years, whereas that which has not been kyanized becomes thoroughly mouldy in 3 years. The difference between the prepared and unprepared wood is likewise seen when they are placed under a gutter. Kyanized calico remains unaltered for three months in a damp cellar; unkyanized cotton similarly circumstanced falls to pieces when unrolled. The intimate combination of the corrosive sublimate with the texture also prevents it from evaporating, and thereby exerting a poisonous action. (Faraday, *Polyt. J.* 50, 299.) There is however a danger of poisonous effects in steeping the wood, and also in its subsequent use as fuel. (Gm.)

Steeping the wood successively in different *liquids, which decompose each other, and yield an insoluble substance which fills the cells.* First green vitriol, then crude acetate of lime. By this treatment, gypsum, and perhaps afterwards sesquioxide of iron, is fixed in the wood, while the acetic acid is washed out or evaporates. This process is said to yield good results.—First protochloride of copper, afterwards carbonate of soda or milk of lime; the latter does not however penetrate well. (Treffy, *Polyt. J.* 72, 461.)—It might be useful also to try green or blue vitriol, and then a solution of alkaline silicate (soluble glass, III., 371). The

wood would be thereby penetrated with a metallic silicate, and petrified to a certain extent.—Or: Blue vitriol, then chloride of calcium, then soluble glass. By this process gypsum would be deposited as well as silicate of copper; also silicate of lime, if the quantity of soluble glass were larger.—First, oil of vitriol, then a solution of resin in aqueous potash.

Coating or saturating the wood with *Resinous* or *Fatty Substances*, which keep out air and water. Repeated rubbing-in of coal-tar or wood-tar (the latter is not so good as the former); or a solution of common resin in oil of turpentine, train oil, or any other fat. (*Polyt. J.* 4, 480; 27, 185; 40, 218; 56, 152.)—Saturation with a fixed oil, such as train oil; with a solution of litharge in linseed oil; with a solution of pitch, sulphur, and wax in train oil, &c. (*Polyt. J.* 37, 152; 40, 218.)

Small boards of *Pinus sylvestris*, 2 lines thick, 1 inch wide, and 4 inches long, were macerated in a solution of 1 pt. of either of the following salts in 25 parts of water; Priestley's substance was produced only in the alum-solution. A portion of these boards cut into shavings, and repeatedly boiled with water, gave up a portion of the salt to the water; but the boiled shavings yielded an ash containing alumina and one of the fixed heavy metallic oxides. The soaked boards, together with one which had not been so treated, were buried in the garden under the northern eaves of a house. After two years the boards exhibited the following characters: Wood, in its ordinary state, not steeped: brownish, rotten.—2. With alum: like 1.—3. With sulphate of manganese: like 1.—4. With protochloride of tin: like 1.—5. With nitrate of lead: somewhat firmer.—6. With blue vitriol: less brownish, solid.—7. Corrosive sublimate: more reddish than brownish yellow, and still more solid than 6.—Linen saturated with these solutions, then placed in a large dish, and buried in garden-mould, which was situated in a sunny place, and often copiously watered, disappeared completely, even when saturated with corrosive sublimate.

When the strips of linen were steeped in rather strong solutions, buried in the garden-mould in such a manner that the end of the strip projected out, and otherwise treated as above for nine months, the following effects were produced: Linen in its ordinary state: the whole disappeared as far as the projecting end, which was brownish white, but still tough; a few light brown, brittle remnants of the portion which had been covered with earth, still adhered to it.—2. With sulphate of manganese; like 1.—3. With sulphate of zinc: like 1, excepting that somewhat more of the buried portion remained in a brown, brittle state.—4. With protochloride of tin: none of the strip had disappeared, but it was for the most part brown and brittle.—5. Green vitriol: like 1.—6. Pyrolignate of iron: like 1.—7. Blue vitriol: almost unaltered, white and tough: the lowest part alone was somewhat brown and brittle.—8. Protochloride of copper: completely preserved, white, with a tinge of green (a proof of the fixation of the copper), perfectly tough and solid.—9. Corrosive sublimate: the lower part had disappeared; the upper portion was white, tough, and completely preserved; the middle, brownish and brittle.—10. Creosote: like 1.—The superior preserving power of the copper-salts above that of the corrosive sublimate may perhaps be due to the greater solubility of the former, which enables them to be used in a more saturated solution. (Gm.)

At all events, these experiments show that the greatest preservative power is exerted by corrosive sublimate, blue vitriol, and chloride of copper. The high price and excessively poisonous properties of corrosive

sublimate render it highly desirable that experiments should be made on the large scale, with the view of testing the efficacy of one of these copper-salts in place of corrosive sublimate for steeping the sleepers of railways. (Gm.)

Method of saturating Wood with the above-mentioned Liquids.

1. *Continued immersion of the wood in cisterns filled with the liquid.*—The liquid does not diffuse itself uniformly; it is prevented by the enclosed air from penetrating the wood; and portions of the wood are left unimpregnated, larger in proportion as the time of immersion is shorter and the liquid is less mobile.

2. *Boucherie's process.*—A tree is stripped in summer of a portion of its branches, leaving only the terminal boughs; a hole is bored horizontally through the stem above the soil, and the tree sawn through right and left from this hole, leaving only a portion an inch thick on each side entire. The whole section, excepting the opening of the bore-hole, is then wrapped round with a tarred cloth, and the aperture immediately connected with a vessel containing the liquid. Rapid absorption then takes place (in large trees to the amount of 200 or 300 litres); the liquid rises quickly in the stem (in a poplar it rose 30 metres in 7 days), driving the sap before it into the twigs and leaves, and freeing the wood from all substances which would give it a tendency to putrefy; and in 10 days penetrates the stem throughout, excepting the innermost part, which has already lost a great part of its vitality. Boucherie chiefly uses crude acetate of iron (1 pt. of which in the dry state suffices for 50 parts of wood), sometimes with the addition of chloride of calcium, because the former when used alone makes the wood very hard and difficult to work. [Copper-salts or corrosive sublimate, which Boucherie also more lately used, would exert a still greater antiseptic action.] If ferrocyanide of potassium be made to rise in the stem after the iron-salt, the wood acquires a blue colour; and other colours may be produced by similar means. Vegetable liquids penetrate less easily, probably because the atoms of organic compounds are larger. (Boucherie, *Ann. Chim. Phys.* 74, 113; also *J. pr. Chem.* 21, 445.)

Transverse sleepers for railways, formed of oak, beech, white beech, birch, alder, with the sap in them, when saturated by this process, either with blue vitriol, or with a mixture of corrosive sublimate and common salt, or with *Chlorure de calcium pyrolignité* (a mixture of chloride of calcium and crude acetate of iron), and buried in the ground for three years, were found to be quite unaltered, or even harder than at first; while similar sleepers in the unprepared state suffered in the same time a considerable degree of putrefaction, and were softened on the surface. (Boucherie, *Compt. rend.* 21, 1153.)

3. *Bréant's process.*—The pieces of wood are enclosed in a metal cylinder and surrounded with the liquid, which is forced into the wood by means of the air-pump or of steam, the air disengaged from the wood being suffered to escape from the upper part of the cylinder by a safety-valve. By this treatment the wood becomes completely penetrated by the liquid, excepting the knots and resinous parts. Wood saturated in this manner with linseed oil keeps remarkably well; but when saturated with green vitriol, it is brittle, and not well adapted for use. (From the Reports of the Soc. d'Encouragement, 1840. Decemb. in the *Revue scient.* 4, 273.).

Preservation of Vegetables.

1. Salting.
2. Drying.
3. By Appert's process (p. 100). Effective, but rather troublesome.
4. According to Braconnot. (*Ann. Chim. Phys.* 64, 170; also *J. chim. méd.* 13, 442; also *J. pr. Chem.* 11, 375.) A cask provided with a door is three-fourths filled with sorrel, lettuce, endive, chicory (even if rancid), or asparagus; and a piece of a rag steeped in sulphur and attached to the end of a wire is set on fire and introduced through the door, the contamination of the vegetables by the falling down of the burnt matter being prevented by laying a board upon them; the door is then closed, and the cask agitated to accelerate the absorption of the sulphurous acid. The sulphuring is twice more performed in the same manner, and the vegetables, together with the liquid which has oozed from them, are put into stoneware jars, which are then merely tied round with parchment and put into a cellar. Vegetables thus treated keep well till the April of the following year. They do not however soften so quickly in water as fresh vegetables, and must therefore, before boiling, be soaked in cold water for some hours (asparagus in April for 24 hours). During the boiling, which generally does not last longer than with fresh vegetables, the sulphurous acid is given off. This method is applicable only to tender vegetables, which easily soften in boiling.

Preservation of Eggs.

Eggs immersed while fresh in milk of lime, will keep in it for years, doubtless because the carbonate of lime formed by the carbonic acid evolved from the egg, completely stops up the pores of the shell. On pulling down a sacristy in the neighbourhood of *Lago Maggiore*, eggs were found quite fresh, after having been surrounded with mortar and enclosed in a wall for 300 years. (*J. Pharm.* 7, 457.)

Preservation of Meat intended for consumption.

1. *Freezing temperature.*—In Canada, cattle whose flesh is intended for winter consumption, are slaughtered as soon as the frost sets in, and the meat is kept in the frozen state.
2. *Drying.*—The well-known process adopted in South America.
3. *Appert's process* (p. 100).—Pieces of meat likewise keep for several weeks when immersed in well-boiled water covered with oil. (Sweny.)
4. *Nitric oxide gas.*—This gas is passed into a vessel filled with the meat, and the vessel well closed; the hyponitric acid thus formed turns the meat brown. (Guepin, *J. chim. méd.* 11, 545; Lippack, *Jahrb. prakt. Pharm.* 1, 23.) This preservative power of nitric oxide gas was discovered by Priestley. (*Exp. and Obs. on diff. kinds of air*, 1, 123.) After Priestley, Hildebrandt (p. 105), and Braconnot (*J. chim. méd.* 7, 708), showed that nitric oxide gas and vapour of hyponitric acid protect meat from putrefaction.
5. *Chlorine.*—Meat which has been exposed to the vapours of chloride of lime, will keep for any length of time. (Braconnot.)—Beef, placed for a few minutes in contact with chlorine gas, and then hung up in the air, will keep for six months; only it becomes perfectly dry. Putrid meat

immersed in chlorine-water, loses its bad smell and assumes the appearance of fresh meat. (Raimond, *J. Pharm.* 4, 426.)

6. Pickling with *Common Salt* and *Nitre;* sometimes with the addition of pounded sugar.

7. *Injection with Hydrochlorate of Alumina.*—The carotid artery and jugular vein of an ox just killed by the pole-axe, are opened; the two extremities of the jugular vein and the upper end of the carotid artery are tied, after the blood has ceased to flow; and the lower end of the carotid artery connected by means of a flexible tube with a syringe, by means of which a solution of 2 kilogrammes of chloride of aluminum in 10 kilogrammes of water is rapidly injected, till the superficial veins appear fully distended. Lastly, the flexible tube is taken between the fingers and pressed from above downwards, in order to force in more liquid; the carotid artery is tied; the syringe removed; the skin of the animal stripped off after 20 minutes; the entrails taken out; and the carcase cut up. The different parts of the body exhibit the usual appearances, excepting that the lungs appear of a paler colour than usual. Meat thus prepared will keep in the air, provided flies be kept off, for 4 weeks in winter, and in summer, in a cool airy place, for 2 weeks. If required to be kept longer, it must be washed with a mixture of equal parts of a solution of common salt of 10° Bm., and the above solution of 1 pt. chloride of aluminum in 5 water, to remove coagulated blood and mucous matters; then pressed down into casks, till the casks are quite full; another portion of the mixture of common salt and chloride of aluminum poured in; and the casks securely closed. Flesh thus treated keeps well for a quarter of a year. Or the meat, after having been washed with the mixture of common salt and chloride of aluminum, is dried either in a current of hot air, or by smoking, and afterwards kept in casks closed air-tight. Before use, it is macerated for 24 hours in water or salt and water. (Gannal, *Revue scientif.* 5, 183; abstr. *Compt. rend.* 12, 532; also *J. pr. Chem.* 23, 305.)

8. *Smoking.*—By this treatment, the meat becomes impregnated with acetic acid and empyreumatic oils and resins, which exert an antiputrescent action; among these substances, creosote appears to play the principal part. A similar result is produced by immersing the meat in an aqueous infusion of pounded *Glanzruss* (p. 85), or in dilute creosote-water, whereby it acquires the taste and smell of creosote. But if a basin containing creosote be placed near the meat, in summer, and a cover put over both, the meat will keep in the atmosphere of creosote four days longer than under ordinary circumstances, and yet will not taste of creosote after boiling. (Stenhouse, *Glasgow Phil. Soc.* 1, 145.) Monge, Meinecke, and Berres recommend pyroligneous acid; meat, after immersion in this liquid, dries in the air without putrefying, but is not very palatable.

Preservation of Corpses and Anatomical Preparations.

Aqueous Sulphurous acid, first recommended by J. Davy, is very efficacious; it does not destroy the muscular fibre, but in the course of five months, converts the cellular tissue and tendons into a transparent jelly. Parts of the animal body keep longer than 4 weeks, if surrounded with tow which is impregnated with sulphurous acid. (Taufflieb, *J. Pharm.* 18, 452.)—Ox-blood also, agitated with air in which sulphur has been

burned, remains unaltered for at least four weeks. (Pontet, *Bullet. Pharm.* 3, 557.)

Sulphuric acid.—Corpses immersed for a few hours in water containing sulphuric acid, keep for 14 days without any signs of putrefaction. (Soubeiran, *J. Pharm.* 18, 456.)

Corpses, which are to be kept for future legal investigation, may be injected (avoiding the use of heavy metallic salts), according to Sucquet, with *sulphite of soda;* according to Bobière (*Compt. rend.* 22, 272) with *sulphate of soda;* according to Gannal (*J. chim méd.* 11, 367) with a solution of 1 lb. of nitre, 2 lb. common salt, and 2 lb. alum in 40 lb. water.—For animals to be kept for stuffing, Gannal (*J. chim. méd.* 20, 53) uses sulphate of alumina mixed with an aqueous docoction of *Nux vomica.*—Macartney keeps anatomical preparations in a solution of nitre and alum.

Solutions of common salt, nitre, alum, or sulphate of zinc afford but partial protection against the decomposition of anatomical preparations. In a solution of ferric sulphate, as recommended by Braconnot, they become covered with a yellow crust of basic ferric sulphate, which makes it difficult to recognise them; the liquid at the same time becomes decolorized, from formation of ferrous salt. Corrosive sublimate decolorizes anatomical preparations, hardens them, and renders them undistinguishable. The liquid best adapted to the purpose is a solution of 1 pt. bichloride of tin in 20 water, acidulated with a small quantity of hydrochloric acid. In this solution, the different parts of the animal body preserve their peculiar consistence and aspect, excepting that the muscular flesh becomes somewhat brownish. But preparations containing bones, must first be immersed for a while in water acidulated with hydrochloric acid, to dissolve out the lime-salts which would precipitate the oxide of tin. Muscular flesh which has been kept in the tin-solution does not putrefy on subsequent exposure to the air, but gradually dries up. (Taufflieb).

Anatomical preparations and corpses freed from the viscera, if macerated in a concentrated solution of corrosive sublimate, and then exposed to the air, dry up to an unalterable mass, in which the muscular flesh is almost as hard as wood. (Chaussier.)—The action of corrosive sublimate depends upon its forming chemical compounds with fibrin and albumen. (Lassaigne.)—Ferric sulphate may perhaps save from putrefaction the finger of a child's corpse, but not a whole body. An alcoholic solution of corrosive sublimate affords complete protection. (Deschamps, *J. chim. méd.* 5, 32.)—An alcohol solution of corrosive sublimate has much greater preserving power than the aqueous solution, because it penetrates the dermis and epidermis much more readily. When the aqueous solution is used, it is necessary to make numerous incisions in the skin, to fill the intestinal canal and the thoracic and abdominal cavities with the saturated solution, and to take out the brain, which will not keep in the aqueous, but only in the alcoholic solution. (Pelletan, *J. chim. méd.* 5, 54.)

To preserve corpses for several years, Tranchina injects into the aorta 24 lb. of alcohol, through which is diffused a mixture of 1 lb. arsenious acid with 1½ oz. red-lead or cinnabar in a state of minute division.—Corpses thus treated may give off arseniuretted hydrogen. (Hünefeld, *J. pr. Chem.* 16, 155.) It is sufficient to boil from 60 to 125 grammes of arsenious acid with 1500 grammes of water, and inject this solution with

some force, by means of a common enema-syringe, which should not be greasy, into the carotid or crural artery, and if the corpse is to be kept as long as possible, to repeat this operation twice more in the course of a few hours. The corpse thus treated with arsenious acid gradually dries up, and, as no putrefaction takes place, no arseniuretted hydrogen can be formed; the brain appears quite sound after the lapse of several weeks. This injection likewise serves for anatomical preparations, the muscles remaining of a deep red colour; bones and ligaments are also protected from the attacks of insects by dipping them into warm arsenious acid. (Dujat, *J. chim. méd.* 16, 81.)—Gannal also uses arsenious acid in large quantities for embalming corpses. (Moian, *J. chim. méd.* 21, 645 and 648; 22, 14 and 68.)

Corpses freed from the viscera may be preserved for a while by washing with chloride of lime, or sprinkling with a solution of creosote in wood-vinegar. (Landerer, *Repert.* 53, 405.)

In place of the spirit commonly used for preserving anatomical preparations, Bobière (*Compt. rend.* 22, 672) uses a mixture of 1 pt. wood-spirit and 3 water; Gaznaga (*J. chim. méd.* 20, 55) the liquid obtained by distilling a mixture of equal parts of brandy obtained from grain (British brandy) and oil of turpentine.

Jacobson (*Hamb. Mag.* 1833, Jan. 48) recommends for anatomical preparations a solution of 1 pt. chromate of potash in 256 pts. water.

Flesh immersed in treacle becomes mummy-like and unalterable. (Mackenzie, *Edinb. Med. and Surg. J.* No. 96, 34.)

Tannin likewise protects flesh from putrefaction. (J. Davy.)

It is well known that corpses buried in very warm dry earth, dry up to mummies without putrefying.

5. *Decompositions by Chlorine, Bromine, and Iodine.*

Chlorine decomposes organic compounds containing hydrogen chiefly by its strong affinity for that element. It acts for the most part even at ordinary temperatures; but the action is greatly assisted by light and heat.

a. It withdraws hydrogen from many compounds rich in that element, producing an evolution of heat which sometimes rises to fiery combustion, the carbon being separated in the form of finely divided soot; in some cases, the action of light or of an elevated temperature is required to induce the fiery decomposition.

Marsh-gas mixed with chlorine at ordinary temperatures exhibits fiery explosion and deposition of soot; if a large quantity of carbonic acid is likewise present, and the action thereby weakened, decomposition takes place quietly by substitution.—Olefiant gas mixed with chlorine, is decomposed on the approach of a lighted taper, producing a red flame darkened by smoke.—A similar flame is produced on introducing a wax taper into chlorine gas.—Bubbles of chlorine gas passed through alcohol, heat it at first, and if the vessel be placed in the sunshine, may also produce fiery detonations and formation of soot. Ether is affected by chlorine in a similar manner.—Oxide of cacodyle burns in chlorine gas even at ordinary temperatures, with deposition of soot.

b. In most cases, chlorine abstracts hydrogen from organic compounds without production of fire; and when that is the case, there is no deposi-

tion of soot, because all the carbon remains in the altered compound. This decomposition is likewise favoured by light and heat. The hydrochloric acid formed in the reaction may then act on the organic compound in its own way.

a. The organic compound loses all its hydrogen, and is resolved into a number of inorganic compounds.—Formic acid, $C^2H^2O^4$, by taking up 2Cl, is converted into $2CO^2$ and 2HCl.

β. Or only a part of the hydrogen is removed, and the chlorine does not enter into the organic compound.—Chlorine gas passed through alcohol diluted with 2 parts of water, forms nothing but aldehyde and hydrochloric acid:

$$C^4H^6O^2 + 2Cl = C^4H^4O^2 + 2HCl.$$

Benzoin, $C^{28}H^{12}O^4$, is converted by chlorine into benzoyl, $C^{28}H^{10}O^4$.

γ. Or the number of atoms of chlorine which enter into the compound is less than the number of atoms of hydrogen withdrawn.—Alcohol, $C^4H^6O^2$, by the action of 8Cl, is ultimately converted into chloral, $C^4HCl^3O^2$ and 5HCl.

δ. Or the atoms of hydrogen withdrawn are replaced by an equal number of atoms of chlorine (p. 73). The following are additional examples: Marsh gas, C^2H^4, is converted by 8Cl—provided fiery decomposition be prevented—into chloride of carbon, C^2Cl^4 and 4HCl.—Chloride of methyl, C^2H^3Cl, is converted by chlorine, in sunshine, first into $C^2H^2Cl^2$, then into C^2HCl^3, and lastly into C^2Cl^4.—Ether, C^4H^5O, is converted by the continued action of chlorine, first into C^4H^4ClO, then into $C^4H^3Cl^2O$, and finally into C^4Cl^5O.—Acetic acid, $C^4H^4O^4$, is converted into chloracetic acid, $C^4HCl^3O^4$; butyric acid, $C^8H^8O^4$, first into $C^8H^6Cl^2O^4$, afterwards into $C^8H^4Cl^4O^4$; valerianic acid, $C^{10}H^{10}O^4$, into chlorovalerianic acid, $C^{10}H^7Cl^3O^4$; saligenin, $C^{14}H^8O^4$, first into $C^{14}H^7ClO^4$, then into $C^{14}H^6Cl^2O^4$, and lastly into $C^{14}H^5Cl^3O^4$; salicylous acid, $C^{14}H^6O^4$, into chlorosalicylous acid, $C^{14}H^5ClO^4$; salicylic acid, $C^{14}H^6O^6$, into bichlorosalicylic acid, $C^{14}H^4Cl^2O^6$; cuminol, $C^{20}H^{12}O^2$, into chlorocuminol, $C^{20}H^{11}ClO^2$.

ε. Or the atoms of hydrogen withdrawn are replaced by a larger number of atoms of chlorine.—Olefiant gas, C^4H^4 mixed with 2Cl, condenses to an oil $C^4H^4Cl^2$; but by the action of a larger quantity of chlorine in sunshine, it is transformed into C^4Cl^6.—Toluol, $C^{14}H^8$, exposed to the continual action of chlorine, aided by light, is converted into $C^{14}H^6Cl^4$ ($=C^{14}H^5Cl^3,HCl$), then into $C^{14}H^5Cl^7$ ($=C^{14}H^3Cl^5,H^2Cl^2$), and $C^{14}H^4Cl^8$ ($=C^{14}H^3Cl^5,H^3Cl^3$). In most of these cases, it is probable that the substitution really takes place in equal numbers of atoms, but that the resulting compound retains, in addition, either 2Cl, or H and Cl in equal numbers of atoms (pp. 71, 72).

ζ. Or chlorine simply enters the organic compound without elimination of hydrochloric acid, so that it appears as though the new substance were simply a compound of the original substance with two or more atoms of chlorine.—Olefiant gas, C^4H^4, forms with 2Cl the oil of olefiant gas, $C^4H^4Cl^2$ ($=C^4H^3Cl,HCl$).—Benzol, $C^{12}H^6$, with 6Cl, forms chlorobenzin, $C^{12}H^6Cl^6$ ($=C^{12}H^3Cl^3,H^3Cl^3$).—Naphthalin, $C^{20}H^8$, is converted by 4Cl into $C^{20}H^8Cl^4$ ($=C^{20}H^6Cl^2,H^2Cl^2$). But when these three chlorine-products are treated with alcoholic solution of potash, the first loses 1 At., the second 3 At., and the third 2 At. of hydrochloric acid; so that there remains a residue in which the substitution has taken place in exact proportion, viz., C^4H^3Cl; $C^{12}H^3Cl^3$; $C^{20}H^6Cl^2$. In some cases, the same effect is produced by

heat, hydrochloric acid escaping. Hence it is probable that these products are not formed directly by the combination of the organic substance with chlorine; but that the chlorine, as in former cases, displaces a certain number of hydrogen-atoms in the substance, these hydrogen-atoms, however, not being removed from the substituted compound, but remaining externally attached to it, together with an equal number of chlorine-atoms. These external atoms of chlorine and hydrogen are perhaps not united in the form of hydrochloric acid, but attached to the nucleus at different points; for the alcoholic solution of the above-mentioned chlorine-products does not precipitate nitrate of silver. On treating the compound with potash, the chlorine and hydrogen are removed in the forms of chloride of potassium and of water, the potash, however, exerting no action on the chlorine in the remaining compound, C^4H^3Cl, &c. Probably, therefore, the correct formulæ of these compounds are those which are above inclosed within brackets. It has already been observed (pp. 20, 21), that Laurent, who formerly regarded this view as the right one, has lately admitted the existence of direct chlorine-compounds, and therefore writes, for example, not $C^{20}H^8Cl^8,H^2Cl^2$, but $C^{20}H^8Cl^4$. The observations just made apply also to the chlorine-compounds of toluol mentioned under *e*. In the chlorine-compound C^4Cl^6, formed from C^4H^4, it must, however, be likewise admitted that 2 At. Cl have attached themselves to the substitution-product, C^4Cl^4.

Kane (*N. Ann. Chim. Phys.* 2, 152) supposes that the destruction of many vegetable colours, those of lichens, for example, by chlorine, is due, not to the abstraction or indirect oxidation of their hydrogen but to the formation of a brown compound by the direct combination of the chlorine with the colouring matter.

It is only in a few compounds that chlorine is capable of replacing the whole of the hydrogen. Many hydrogen-atoms appear to be so placed in the compound-atom, that the attraction of the other atoms, especially of the oxygen-atoms, which have a strong affinity for the hydrogen and but a feeble affinity for the chlorine, prevents the substitution. This circumstance may perhaps give an insight into the probable relative position of the atoms.

In some cases, chlorine exerts an indirect oxidizing action by taking up the hydrogen of the water which is present, and transferring its oxygen, either to the entire organic compound, or to its carbon and hydrogen. This may perhaps explain why so many compounds are not decomposed by chlorine when water is entirely excluded.

Perfectly dry litmus-paper does not lose its colour in dry chlorine gas.—Chlorine, in presence of water, acts upon indigo-blue, $C^{16}H^5NO^2$, first transferring to it 2 At. of oxygen from the water, and converting it into isatin, $C^{16}H^5NO^4$, which is then immediately transformed by substitution, into chlorisatin, $C^{16}H^4ClNO^4$, and bichlorisatin, $C^{16}H^3Cl^2NO^4$.—Similarly, chlorine, in presence of water, converts bitter almond oil, $C^{14}H^6O^2$, into benzoic acid, $C^{14}H^6O^4$, and cuminol, $C^{20}H^{12}O^2$, into cuminic acid, $C^{20}H^{12}O^4$, hydrochloric acid being formed at the same time.—Aqueous saligenin, $C^{14}H^8O^4$, is for the most part converted by chlorine into chlorophenissic acid, $C^{12}H^2Cl^2O^2$, 2 At. carbon appearing to be expelled in the form of carbonic acid.

On these decompositions and transformations of most organic compounds by chlorine, depends its power of destroying many organic colouring matters, or turning them pale brown, and consequently its

application in bleaching; also its power of converting many colourless organic compounds, the alkaloids, for example, into coloured compounds; and of removing or changing the smell of odoriferous organic compounds and destroying miasmata and contagious matters: in consequence of this latter property, it is used for fumigation and washing, being, in fact, the most efficacious of all smell-destroying and anti-miasmatic agents.

But few organic compounds withstand the action of chlorine; among those which do so, are succinic and mucic acid; tartaric acid also scarcely exhibits any sign of decomposition.

Bromine acts in a very similar manner to chlorine, but less energetically, because its affinity for hydrogen is not so great. Hence only a few organic substances—alkarsin among the number—are set on fire by bromine at ordinary temperatures; and in many compounds it does not replace so many atoms of hydrogen as chlorine does. But it forms many bromine-compounds corresponding to the chlorine-compounds, part of the hydrogen being replaced by bromine.

Iodine acts in a precisely similar manner to chlorine and bromine; but its affinity for hydrogen being much less, its decomposing action on organic compounds is likewise much less powerful; hence no organic compound appears to be set on fire by it at ordinary temperatures, although it acts violently on many volatile oils, producing great rise of temperature. Many compounds which are decomposed by chlorine or bromine, either resist the action of iodine, or are very slowly attacked by it; hence it is very slow in its action on vegetable colours. The brown colouring which iodine imparts to many organic compounds, *e. g.*, to paper, to the epidermis, &c., proceeds from the formation of hydriodous acid, HI^3.

When bromine or iodine acts upon an organic compound in presence of potash and water, it frequently yields bromoform, C^2HBr^3, or iodoform, C^2HI^3, besides other products. Thus, wood-spirit with potash and bromine, and citrate or malate of potash with bromine, yield bromoform. —Iodoform is produced by the action of iodine in presence of aqueous potash, upon wood-spirit, alcohol, sugar, gum, protein-compounds, &c.

In other cases, bromine and iodine, in presence of aqueous potash, act merely by indirect oxidation. In this manner they convert fusel-oil into valerianic acid, and produce salicylous acid from salicin, and oil of bitter almonds from amygdalin. (*Comp.* Cahours, Millon and Lefort, *Compt. rend.* 21, 814 and 828; 23, 229.)

6. *Decompositions by Nitric Acid.*

Very few organic compounds, *e. g.*, fumaric, succinic, euchronic, valerianic, suberic, pyromucic and camphoric acid, paraffin and hatchettin, withstand the action of nitric acid; in other organic compounds, this acid produces changes of various kinds.

a. Substitution.—One or more atoms of H are replaced by an equal number of atoms of NO^4 or X (p. 73). Concentrated nitric acid is the best for this reaction; it must, however, be free from nitrous acid, which even oxidizes carbon. The transformation sometimes takes place at ordinary temperatures, and is attended with evolution of heat, as with cinnamic acid; sometimes a boiling heat is required; it is not attended with evolution of gas.

b. Oxidation of the Organic Compound, without decomposition.—Aldehyde, $C^4H^4O^2$, heated with nitric acid, is converted into acetic acid, $C^4H^4O^4$; cacodyl, C^4H^6As, into oxide of cacodyl, C^4H^6AsO, and afterwards into cacodylic acid, $C^4H^6AsO^4$; bitter almond oil, $C^{14}H^6O^2$, into benzoic acid, $C^{14}H^6O^4$; and œnanthol, $C^{14}H^{14}O^2$, into œnanthylic acid, $C^{14}H^{14}O^4$; cuminol, $C^{20}H^{12}O^2$, is converted, by slow addition of strong nitric acid, into cuminic acid, $C^{20}H^{12}O^4$; camphor, $C^{20}H^{16}O^2$, by long boiling with strong nitric acid, into camphoric acid, $C^{20}H^{16}O^8$; and indigo, $C^{16}H^5NO^2$, by heating with dilute nitric acid, into isatin, $C^{16}H^5NO^4$. The organic compound is thus brought to a higher state of oxidation; thus, the benzoic acid first formed from bitter almond oil, is converted into nitrobenzoic acid.

c. Nitric acid converts 1 or 2 At. H of the compound into water, without substitution. Thus, it converts indigo-white, $C^{16}H^6NO^2$, into indigo-blue, $C^{16}H^5NO^2$; alloxantin, $C^8H^5N^2O^{10}$, into alloxan, $C^8H^4N^2O^{10}$; similarly, alcohol, $C^4H^6O^2$, into aldehyde, $C^4H^4O^2$; fusel-oil, $C^{10}H^{12}O^2$, into valeral, $C^{10}H^{10}O^2$; borneol, $C^{20}H^{18}O^2$, into common camphor, $C^{20}H^{16}O^2$; benzoin, $C^{28}H^{12}O^4$, into benzyl, $C^{28}H^{10}O^4$.

d. The nitric acid abstracts hydrogen, and transfers oxygen to the organic compound.—Of this nature is the conversion of wood-spirit, $C^2H^4O^2$, into formic acid, $C^2H^2O^4$; of alcohol into acetic acid; and probably also the resinizing of many volatile oils by nitric acid.

e. Most organic compounds are more completely decomposed by nitric acid, the oxygen of the acid abstracting from them carbon as well as hydrogen, and forming therewith carbonic acid and water.—This decomposition takes place with greater rapidity in proportion as the acid is hotter and more concentrated, and contains a greater quantity of hyponitric acid, doubtless because the greater affinity of water for nitric acid, holds its constituents more firmly together.—Many compounds, such as succinic acid and urea, resist the action of pure nitric acid, but are decomposed by that acid when it contains hyponitric acid, carbonic acid being evolved. Other compounds are, indeed, decomposed by nitric acid free from hyponitric, but very slowly at first; but since this action is attended with the formation of nitric oxide, which converts a portion of the nitric acid into hyponitric (II., 383), and the quantity of the latter goes on continually increasing, the decomposition may sometimes become very violent. This may be avoided, in many cases, by adding to the mixture nitrate of urea (Millon), on which the hyponitric acid, as it is produced, exclusively acts; and inasmuch as this reaction yields no nitric oxide, but only nitrogen and carbonic acid, the liquid is thereby maintained perfectly free from hyponitric acid.

Those organic compounds which are comparatively rich in oxygen, such as sugar and many of the acids, are, for the most part, more quickly decomposed by nitric acid than those which contain less oxygen or none, because the oxygen already present in them assists in the formation of carbonic acid and water. On the other hand, solid fats, resins, many camphors and certain volatile oils, are but slowly decomposed. But on many volatile oils and on fixed oils, concentrated nitric acid, especially if it be fuming and mixed with oil of vitriol, exerts so rapid a decomposing action, that the evolution of heat, attending on the formation of water and carbonic acid, is often so great as to produce vivid combustion.

As the nitric acid in this oxidizing action loses oxygen, it is partly converted into nitric oxide and nitrogen which escape, and partly gives up its nitrogen to the constituents of the organic matter, forming with

the hydrogen, ammonia, which remains in the residue as nitrate of ammonia or some other ammoniacal salt, and with the carbon and hydrogen, hydrocyanic acid, C^2NH, which goes off in vapour.

Ammonia is therefore not the only product formed by the decomposition of nitrogenous substances, many compounds free from nitrogen being in fact obtained at the same time. Resin, sugar, phloridzin, humic acid, and charcoal, treated with nitric acid, often yield crenate or apocrenate of ammonia. (Mulder, *J. pr. Chem.* 33, 345.)—The liquid obtained in the decomposition of oil of turpentine or juniper by dilute nitric acid yields on evaporation, quadroxalate of ammonia. (Rabourdin, *N. J. Pharm.* 6, 187.)

Hydrocyanic acid appears to be produced in the distillation of most organic substances with nitric acid, and has been obtained by the application of this treatment to the serum of blood, sugar, gum, starch, alcohol, volatile oils, resins, fats, vegetable acids, &c. (*vid. Formation of Cyanogen*). According to Sobrero, the formation of hydrocyanic acid is connected with that of ammonia.

As the organic compound loses a considerable portion of its carbon and hydrogen by the formation of carbonic acid and water, it becomes continually richer in oxygen, and is transformed from a compound of a higher order containing a proportionally larger number of atoms of carbon and hydrogen, into one or more compounds of lower order.

If the action of the nitric acid be continued, the final products are generally oxalic acid, C^2HO^4, or $C^4H^2O^8$, acetic acid, $C^4H^4O^4$, and formic acid, $C^2H^2O^4$. The two latter, being volatile, are withdrawn from the further action of the nitric acid; but the oxalic acid, which remains behind, is at length, by the further addition of oxygen from the nitric acid, completely resolved into carbonic acid and water. The formation of oxalic acid is usually preceded by that of saccharic ($C^6H^5O^8$ or $C^{12}H^{10}O^{16}$), but this, by continued action of the nitric acid, is easily converted into oxalic acid.

In this manner, the following substances, when treated with nitric acid, yield oxalic acid as their final organic product of decomposition, generally associated with formic and acetic acid: Alcohol, lactic acid, tartaric, malic, kinic, tannic, gallic, and meconic acid,—many volatile oils and resins,—sugar, gum, starch, woody fibre, indigo, &c.

In some organic compounds, however, the splitting of the nuclei and the abstraction of carbon does not go so far as to leave oxalic acid as the final product; but products are formed, which contain more than 4 At. carbon, and do not further give off carbon, but are often capable of taking up NO^4 by substitution.

Thus stearic acid when subjected to the continued action of nitric acid ultimately yields succinic acid, $C^4H^6O^8$, and suberic acid, $C^{16}H^{14}O^8$, which undergo no further change. Cinnamic acid, $C^{18}H^8O^4$, distilled with nitric acid loses 4C and 2HO, and yields bitter almond oil, $C^{14}H^6O^2$, which, by the further action of nitric acid, is converted, first into benzoic acid, $C^{14}H^6O^4$, and then into nitro-benzoic acid, $C^{14}H^5XO^4$. Similarly, saligenin, $C^{14}H^8O^4$, distilled with concentrated nitric acid, is converted, with formation of carbonic acid, into picric acid, $C^{12}H^3X^3O^2$. Anisol, $C^{20}H^{12}O^2$, treated continuously, first with weak and afterwards with stronger nitric acid, is converted, first into hydranisyl, $C^{16}H^8O^4$, then into anisic acid, $C^{16}H^8O^6$, and lastly, into nitranisic acid, $C^{11}H^7XO^6$.—Many organic mixtures, such as extract of logwood or fustic, fetid gum-resins, &c., when boiled for a long time with nitric acid, yield styphnic acid, $C^{12}H^3X^3O^4$.—The formation of

Hatchett's nitrogenized artificial tannin (a substance decomposible into several compounds of lower orders) which is produced by boiling indigo, various resins, coal or charcoal, with dilute nitric acid, and resembles true tannin in its power of precipitating gelatin,—appears likewise to depend upon the abstraction of part of the carbon and hydrogen contained in these compounds, and the introduction of NO^4 by substitution.—A similar action probably takes place in the formation of the yellow bitter matter (*jaune amer*), which is produced by treating various animal substances with nitric acid, and is related to picric acid, $C^{12}H^3X^3O^2$.—Lastly, the resinous masses obtained by treating many volatile oils and resins with nitric acid are probably formed in a similar manner.

7. *Decompositions by the Acids of Chlorine.*

These acids destroy most organic compounds, sometimes by imparting oxygen to them and giving rise to the evolution of chlorine and carbonic acid, and in the case of nitrogenous bodies, like urea, uric acid, and the alkaloids, also of nitrogen and chloride of nitrogen,—sometimes by giving both oxygen and chlorine to the organic compound.

Thus *Hypochlorous acid* with alcohol forms acetic acid and the oil of olefiant gas. (Balard.)—Hypochlorite of lime distilled with alcohol yields chloroform.—Hypochlorous acid and its salts exert a powerful destroying action on colouring and odoriferous matters.—*Chloric oxide gas*, evolved from chlorate of potash by oil of vitriol, sets fire to alcohol placed in a layer above the mixture.—When organic compounds are placed in contact with a mixture of chlorate of potash and concentrated hydrochloric acid, they are changed in the same manner as if chlorine and oxygen were to act upon them simultaneously. Thus creosote is converted into chloranil:

$$C^{12}H^6O^2 + 10Cl + 2O = C^{12}Cl^4O^4 + 6HCl.$$

Similarly, anthranilic acid into chloranil:

$$C^{14}H^7NO^4 + 8Cl + 4O = 2CO^2 + NH^3 + 4HCl + C^{12}Cl^4O^4.$$

Concentrated *Chloric acid*, or a piece of paper saturated with it, sets fire to alcohol and ether. It destroys most organic compounds, but is much slower in its bleaching action than chlorine or hypochlorous acid. Paper held in the vapour of boiling perchloric acid takes fire; but this acid when distilled with alcohol, acts like oil of vitriol, producing water and ether, without itself undergoing decomposition.

8. *Decompositions by Iodic Acid.*

The deflagration of organic substances by heating them with dry iodic acid has already been mentioned (p. 86).

Aqueous iodic acid exerts no action on many substances even at 100°; *e. g.*, on fats, volatile oils, resins, and other substances insoluble in water, also on acetic acid, butyric acid, camphoric acid, urea, gelatin, or the crystalline lens of the eye. (Millon.)

a. Many organic compounds are raised by iodic acid to a higher degree of oxidation, iodine being set free. Thus it converts fusel-oil into valerianic acid, and oil of bitter almonds into benzoic acid. (Millon.)

b. Other organic compounds are decomposed by iodic acid, for the most part completely, yielding carbonic acid and water, likewise with separation of iodine.—At ordinary temperatures, this decomposition takes place very slowly, and occupies several days; it is accelerated by the presence of spongy platinum or by the action of light; still more by rise of temperature. With many substances, however, complete decomposition does not take place till after several hours' boiling with excess of iodic acid. Ultimately, as much carbonic acid is obtained in this manner, as if the organic compound had been burned with oxide of copper.

With most substances decomposition is prevented, even at 100°, by the addition of a trace of hydrocyanic acid (ferrocyanide or ferricyanide of potassium does not prevent it). Such is the case with oxalic, formic, lactic, tartaric, citric, mucic and meconic acid; also with milk-sugar, common sugar, grape-sugar, dextrin, starch, gum and salicin; among these substances, tartaric acid, citric acid, milk-sugar, salicin, and especially grape-sugar, resist decomposition for the longest time. Other compounds which oxidate very rapidly are completely decomposed by iodic acid, even when hydrocyanic acid is added. Thus: Creosote, gallic acid, tannic acid, morphine, albumen, fibrin and gum. (Millon.)

c. Acetone forms with iodic acid an oily product without separation of iodine.

Comp. Millon (*N. Ann. Chim. Phys.* 13, 57; abstr. *Compt. rend.* 19, 270).

Periodic acid acts in a similar manner to iodic acid (II., 260).

9. *Decompositions by Chromic Acid.*

This acid gives up oxygen to many organic compounds, and is thereby reduced to chromic oxide, or if a mineral acid be present, to a chromic salt.

a. Dry chromic acid instantly sets fire to many organic compounds, at ordinary or at slightly elevated temperatures (p. 86).

Several alkaloids, viz., nicotine, coniine, aniline, chloraniline and leucol, take fire in contact with chromic acid, even at ordinary temperatures; others, such as sinapoline, thiosinnamine, naphthalidam, cinchonine and narcotine, only when they have previously been slightly heated. Oil of mustard, benzol, nitrobenzide, creosote, &c., do not take fire even when heated. The heat evolved in the combination of the chromic acid with the alkaloids probably helps to set them on fire. (A. W. Hofmann, *Ann. Pharm.* 47, 85.)—Alcohol, ether, and œnanthol also take fire when dropped upon crystallized chromic acid.

b. Aqueous chromic acid or a mixture of monochromate or bichromate of potash and dilute sulphuric acid acts on the organic compounds in one of the following ways:

a. Brings it to a higher degree of oxidation.

β. Or withdraws part of its hydrogen.

γ. Or withdraws the hydrogen and puts oxygen in its place.

δ. Or forms water and carbonic acid, and thereby gives rise to the formation of organic compounds of lower order.

Examples of a: Stilbene, $C^{28}H^{12}$, is converted by addition of 4O from the chromic acid into 2 At. of bitter almond oil$=2C^{14}H^6O^2$, which may then by further oxidation be converted into benzoic acid; Œnanthol, $C^{14}H^{14}O^2$, is converted into œnanthylic acid; and indigo-blue into isatin.

Of β: Saligenin, $C^{14}H^8O^4$, is transformed into salicylous acid, $C^{14}H^6O^4$; and fusel-oil, $C^{10}H^{12}O^2$, apparently into valeral, $C^{10}H^{10}O^2$.

Of γ: Toluol, $C^{14}H^{8}$, is converted with difficulty into benzoic acid, $C^{14}H^{6}O^{4}$; fusel-oil, $C^{10}H^{12}O^{2}$, easily into valerianic acid, $C^{10}H^{10}O^{4}$.

Of δ: Tartaric acid, the various kinds of sugar, phloridzin, &c., are converted, by distillation with sulphuric acid and chromate of potash, into water, carbonic acid, formic acid, &c.

¶ Albumen, fibrin, casein, and gelatin treated with bichromate of potash and dilute sulphuric acid, yield a distillate partly acid and partly neutral. The neutral products consist of propionic aldide, $C^{6}H^{6}O^{2}$, and valero-nitrile, $C^{10}H^{7}N$; the acid products are hydrocyanic, formic, acetic, butyric, valerianic and benzoic acid. (Guckelberger, *Ann. Pharm.* 64, 39; *comp.* p. 131.) ¶

Vanadic acid behaves like chromic acid, being reduced to vanadic oxide;—*e. g.*, by alcohol, oxalic acid, tartaric acid, citric acid, and sugar.

Permanganate of Potash acts like chromate of potash. With solution of sugar it forms oxalate of potash. (*comp.* IV., 237.)

10. *Decompositions by Sulphuric Acid.*

A. *By Concentrated Sulphuric Acid.*

The anhydrous acid acts most powerfully; the fuming acid less, and common oil of vitriol still less strongly. The first action of the acid is to dissolve the organic compounds, most of them, at least, considerable rise of temperature taking place at the same time. Subsequently, the sulphuric acid, especially if heat be applied, may produce the following changes in the compounds, even if they are not dissolved:

a. It brings the organic compound into a peculiar isomeric state.—Anise-camphor is converted by oil of vitriol into anisoin.

b. By virtue of its predisposing affinity for water it abstracts hydrogen and oxygen from the compound in equal numbers of atoms, and either leaves a compound comparatively richer in carbon, or causes the residue of the compound left after this abstraction to split up into several new compounds.

Peppermint-camphor, $C^{20}H^{20}O^{2}$, is resolved into menthene, $C^{20}H^{18}$, and 2HO. Oil of vitriol, acting in comparatively small quantity, converts alcohol, $C^{4}H^{6}O^{2}$, into ether, $C^{4}H^{5}O$ and HO; in larger quantity, it transforms the alcohol into olefiant gas, $C^{4}H^{4}$, and 2HO.—It converts fusel-oil, $C^{10}H^{12}O^{2}$, into amylene, $C^{10}H^{10}$, part of it, however, being further decomposed.—Formic acid, $C^{2}H^{2}O^{4}$, treated with oil of vitriol is resolved into 2CO and 2HO, and oxalic acid, $C^{4}H^{2}O^{8}$, into 2CO, $2CO^{2}$ and 2HO.—When imabenzil, $C^{28}H^{11}NO^{2}$, is dissolved in oil of vitriol, it gives up 2HO to the latter; for water subsequently added to the solution throws down benzilam, $C^{28}H^{9}N$.

c. In nitrogenous compounds, it induces by its predisposing affinity the formation of ammonia.—This formation of ammonia takes place with peculiar facility in compounds which contain nitrogen in the form of amidogen. Oxamide heated with oil of vitriol is resolved into sulphate of ammonia, carbonic oxide, and carbonic acid; uric acid into sulphate of ammonia, carbonic oxide, carbonic acid, and sulphurous acid.

d. It gives up its third atom of oxygen to 1 At. hydrogen of the compound, and enters that compound in the form of sulphurous acid,

while the water produced by the decomposition is separated.—(Substitution, p. 74); *e. g.*, Sulphobenzide.

e. With many organic compounds sulphuric acid unites and forms various kinds of *copulated sulphuric acids, q. v.;* the combination being often attended with separation of water.

f. The oxygen of the sulphuric acid not only forms water with the hydrogen of the organic compound, but likewise carbonic acid and carbonic oxide with its carbon. A large proportion of the sulphuric acid is thereby partly converted into sulphurous acid, and partly even reduced to the state of sulphur.—The organic compound, whether it dissolves in the oil of vitriol or not, frequently assumes at first a deep red, orange-yellow, violet or other colour; which, however, if the action of the acid be continued, is converted into brown and black. The volatile decomposition-products, such as formic acid, acetic acid, and furfurol, often produced from the organic compound, pass off together with the mixture of carbonic acid, carbonic oxide, and sulphurous acid gas. The residue generally contains at first a black resin, with which sulphuric acid is intimately combined; also a brown matter which is soluble in water and in alcohol, likewise contains sulphuric acid, and, on account of its property of precipitating gelatin, is called *sulphate of artificial tannin;* often likewise a mouldy substance, and sulphuric acid coupled with an organic compound. If the action of the acid be still further continued, sulphur is often sublimed, and the substances just mentioned unite into a body called *sulphate of carbon* (*Schwefelsaure Kohle*), which is insoluble both in water and in alcohol—likewise contains sulphuric acid, or some other form of sulphur, so intimately combined that it cannot be extracted by alkalis—and is, moreover, distinguished from true charcoal by containing a considerable amount of hydrogen and oxygen. It appears, then, that most organic compounds are *charred* by sulphuric acid.

Cane-sugar, milk-sugar, grape-sugar, starch, lactic acid, tartaric acid, and citric acid, heated with excess of oil of vitriol, become gradually charred, at first giving off pure carbonic oxide gas; and it is only at a later stage of the process—the heat being continued—that this gas becomes mixed with carbonic acid and sulphurous acid; so that the carbonic oxide appears to be formed, not from the oxygen of the sulphuric acid, but from that of the organic compound, in consequence of the decomposition caused by the formation of water. This supposition is corroborated by the fact that compounds consisting wholly of carbon and hydrogen, are capable of yielding large quantities of carbonic acid, but no carbonic oxide.—Fats, most volatile oils, resins, stearic acid, oleic acid, &c., treated with oil of vitriol, form—with evolution of heat—a coloured mixture, which chars when further heated, giving off sulphurous acid, carbonic acid, and frequently also formic acid.—On the contrary, many volatile oils, such as rock-oil, and volatile acids, *e. g.*, caproic, valerianic, and butyric acid, pass off for the most part, undecomposed, when heated with oil of vitriol.—Acetic acid escapes decomposition completely, inasmuch as it volatilizes when heated.

g. Peculiarly remarkable is the production of formic acid and furfurol (a kind of volatile oil) which distil over when saw-dust, bran, flour, starch, or sugar is heated with a mixture of equal volumes of oil of vitriol and water till it begins to char.

Very few organic compounds remain undecomposed when treated with oil of vitriol, especially at a boiling heat; such, however, is the case with mellitic acid.

B. *Action of Dilute Sulphuric Acid.*

Certain other of the stronger acids often exhibit the same action.

a. In some cases, the dilute acid, from some unknown causes, induces the organic compound, at a boiling heat, to take hydrogen and oxygen in equal numbers of atoms from the water, and thereby form a new compound.—Starch, cane-sugar, milk-sugar, and dextrin, boiled with very dilute acids, are converted into grape-sugar.

b. In other cases, on the contrary, it withdraws hydrogen and oxygen from the compound, in equal numbers of atoms.—Saligenin, $C^{14}H^8O^4$, is thus converted into saliretin, $C^{14}H^6O^2$, and 2HO. Saligenin undergoes the same decomposition when heated *per se* above 150°.

c. In amidogen-compounds, it induces, by predisposing affinity, the formation of ammonia and decomposition of water, the oxygen of which passes over to the organic compound.—Oxamide, $C^4H^4N^2O^4$, is resolved with decomposition of 4HO, into oxalic acid, $C^4H^2O^6$, and $2NH^3$; asparagin, $C^8H^8N^2O^6$, with 2HO, into aspartic acid, $C^8H^7NO^6$ and NH^3.—These transformations are likewise produced by water alone; but only at a strong heat, such as can be imparted to the water in sealed glass tubes.

d. Boiling dilute sulphuric acid sometimes, though rarely, causes an evolution of carbonic acid, formed from the oxygen of the organic compound.—Thus, meconic acid. $C^{14}H^4O^{14}$, boiled with dilute sulphuric or hydrochloric acid, gives off $2CO^2$, and is converted into comenic acid.

e. Grape-sugar, boiled for a long time with very dilute sulphuric acid, is converted into a mouldy substance and a small quantity of formic acid.

11. *Decompositions by Phosphoric Acid.*

Anhydrous phosphoric acid acts, by virtue of its water-forming power, like concentrated sulphuric acid; but the decomposition which it causes is much less profound, partly because it has less affinity for water and ammonia, and partly because it retains its oxygen much more tenaciously. It is therefore specially adapted for decompositions in which it is desired to abstract water without producing any stronger action.

By distillation with anhydrous phosphoric acid, which takes up 2 At. HO, alcohol, $C^4H^6O^2$, is converted into olefiant gas, C^4H^4 (a concentrated solution of phosphoric acid likewise forms with alcohol a certain quantity of ether); fusel-oil, $C^{10}H^{12}O^2$, into amylene, $C^{10}H^{10}$, and polymeric compounds of the same; camphor, $C^{20}H^{16}O^2$, into camphene, $C^{20}H^{14}$; borneol, $C^{20}H^{18}O^2$, into borneene, $C^{20}H^{16}$; peppermint-camphor, $C^{20}H^{20}O^2$, into menthene, $C^{20}H^{18}$; ethal, $C^{32}H^{34}O^2$, into cetene, $C^{32}H^{32}$. But oil of bitter almonds, oil of cinnamon, and anise-camphor, do not suffer this decomposition into water and a hydrocarbon, when heated with anhydrous phosphoric acid.—Oxalic acid heated with concentrated phosphoric acid is decomposed in the same manner as with oil of vitriol. Certain compounds, as aldehyde, camphoric acid, and œnanthol, are even blackened by phosphoric acid.

Phosphoric acid likewise transforms certain compounds into others isomeric with them, and forms a few *Copulated Phosphoric acids* (*q. v.*).

12. *Decompositions by Pentachloride of Phosphorus.*

This substance has no action upon hydrocarbons, but acts violently on organic compounds containing oxygen. It generally withdraws 2 At. oxygen from the compound and substitutes 1 At. chlorine for 1 At. hydrogen, so that it is hereby converted into the volatile compound PCl^3O^2 (II., 330).—The alcohols, *e. g.*, wood-spirit, common alcohol, fusel-oil, and ethal, are converted by pentachloride of phosphorus into hydrochloric ethers [chlorides of the radicals]: thus,

Fusel-oil: $C^{10}H^{12}O^2 + PCl^5 = C^{10}H^{11}Cl + PCl^3O^2 + HCl$;
Ethal: $C^{32}H^{34}O^2 + PCl^5 = C^{32}H^{33}Cl + PCl^3O^2 + HCl$.

The pentachloride of phosphorus likewise acts violently on phenous acid and anisol, yielding new products; similarly on benzoic, cinnamic, cuminic and anisic acids. Thus with benzoic acid:

$$C^{14}H^6O^4 + PCl^5 = C^{14}H^5ClO^2 + PCl^3O^2 + HCl;$$

and with anisic acid:

$$C^{16}H^8O^6 + PCl^5 = C^{16}H^7ClO^4 + PCl^3O^2 + HCl.$$

Comp. Dumas & Péligot (*Ann. Chim. Phys.* 62, 14; Cahours, *Compt. rend.* 22, 846).

13. *Decompositions by Metallic Chlorides.*

Chloride of zinc acts, at high temperatures, by formation of water; and, accordingly, like phosphoric acid, it converts alcohol into ether, fusel-oil into amylene, camphor into camphene, &c.

Chloride of antimony and chloride of arsenic act like chloride of phosphorus, the metal withdrawing oxygen from the organic compound, while the chlorine acts upon the residue.—Thus, these chlorides distilled with alcohol yield hydrochloric ether; perhaps in this manner:

$$3C^4H^6O^2 + SbCl^3 = 3C^4H^5Cl + 3HO + SbO^3.$$

14. *Decompositions by Peroxides.*

Of all these compounds, the brown peroxide of lead is most disposed to give up its oxygen to organic compounds; then follows red-lead, and then the peroxides of manganese and nickel.

a. Dry peroxides often produce fiery decomposition; *e. g.*, when peroxide of lead is triturated with tartaric acid, racemic acid, fused citric acid, or effloresced oxalic acid.

b. In presence of water, the chief product is carbonic acid.—Peroxide of lead, even at medium temperatures, converts aqueous tartaric, racemic, or mucic acid into carbonic and formic acid; it likewise decomposes aqueous citric and gallic acid, but without formation of formic acid.—At a boiling heat, it converts sugar into carbonic and formic acid (peroxide of manganese does not decompose sugar); hippuric acid into benzamide, carbonic acid and water; alloxan into urea, oxalic acid and carbonic acid; uric acid into urea, allantoin, oxalic acid and carbonic acid.—Benzoic acid and salicylous acid resist its action, even at a boiling heat.

c. The peroxides of lead, manganese, &c., exert a much stronger oxidizing action when heated with dilute sulphuric acid.—In this manner, oxalic acid is converted into carbonic acid and water; alcohol into aldehyde, formic acid, acetic acid, &c.; sugars, gum, and starch into formic acid, carbonic acid, &c.; tartaric and saccharic acid into formic and carbonic acid; saligenin into the same products (whereas with chromate of potash and dilute sulphuric acid, it yields salicylous acid); kinic acid into chinone; amygdalin into formic acid, bitter-almond oil, ammonia, &c.; narcotine (by peroxide of manganese and sulphuric acid) into cotarnine and opianic acid; and this last substance (with peroxide of lead and sulphuric acid), by simply taking up oxygen, is converted into hemipinic acid.

¶ Albumen, fibrin, casein, or gelatin heated with dilute sulphuric acid and peroxide of manganese, yields a distillate consisting partly of neutral and partly of acid products. With casein, the neutral portion of the distillate consists of the aldides of certain acids of the series $(CH)^nO^4$, viz., common aldehyde, $C^4H^4O^2$, propionic aldide, $C^6H^6O^2$, and butyric aldide, $C^8H^8O^2$, together with oil of bitter almonds; the acid portion, of formic, acetic, propionic, butyric, valerianic, caproic, and benzoic acids. Albumen, fibrin, and gelatin gave the same neutral products, excepting that the first two yielded but small quantities of aldehyde, and the third none; butyric aldide was most abundantly produced from fibrin. The acid products were also similar, with the exception of propionic acid, which was not found; the largest portion of the acid distillate consisted of formic and acetic acid; butyric acid was obtained most abundantly from fibrin, valerianic acid from gelatin; benzoic acid was present in small quantity only.—The chief difference between the action of peroxide of manganese and that of chromic acid on these substances, appears to be that the former yields *Acids, e. g.*, formic and valerianic,—the latter, the *Nitriles* of these acids (*comp.* p. 127); for hydrocyanic acid may be regarded as formic nitrile $[NH^4,C^2HO^4-4HO=C^2HN]$. (Guckelberger, *Ann. Pharm.* 64, 39; abst. *Chem. Gaz.* 1848, 89 and 114; *Jahresber.* 1847–8, 847–854.) ¶

15. *Decompositions by the Basic Oxides of the Heavy Metals.*

Many organic compounds withdraw from basic heavy metallic oxides, presented to them either in the free state or dissolved in acids, the whole or a part of their oxygen, sometimes even in the dark and at ordinary temperatures, sometimes only when exposed to light, especially to direct sunshine, or when heated. The oxygen thus taken up either brings the organic compound to a higher degree of oxidation, or takes away part of its hydrogen, or decomposes it still more completely with formation of carbonic acid.

Many of these decompositions of alcohol and ether which take place only in sunshine, or on the application of heat, and in which the alcohol is probably converted into aldehyde, have been already mentioned (I., 171).

The oxides of the noble metals are reduced with the greatest facility, and in most cases completely. *Bioxide of Osmium* is reduced by alcohol, ether, tannin, epidermis (VI., 407);—*chloriridiate of ammonium* by oxalic acid when exposed to light;—*platinum-salts* by formiates, oxalates, tartrates, alcohol, or sugar (VI., 284).

Of all the metals *gold* is most easily reduced from the teroxide or terchloride, and in general partly to the metallic state, partly to that of the red suboxide (*comp.* VI., 219, 220).

Silver is reduced from the oxide or the nitrate by formic acid, ether, aldehyde, volatile oils, gallic acid, tannin, sugar, &c. If this reduction takes place without evolution of gas, the sides of the vessel become covered with a silver mirror; hence this process may be used for the silvering of glass. For this purpose the following substances are recommended, a solution of nitrate of silver being used, in some cases with addition of ammonia: Aldehyde, saccharic acid, pyromeconic acid, oil of cinnamon, cloves, or pimento, dissolved in alcohol (an alcoholic solution of oil of turpentine, or bay-oil, or of guaiac resin acts less quickly), grape-sugar, which acts even at ordinary temperatures, common sugar, on the application of moderate heat, and gum-arabic, starch, salicin, and phloridzin, which act only after long boiling (*comp.* Stenhouse, *Phil. Mag. J.* 26, 175; also *Ann. Pharm.* 54, 102; also *J. pr. Chem.* 35, 143; see also VI., 143).

In some few organic sulphur-compounds, the sulphur is replaced by the oxygen of the silver-oxide, sulphide of silver being formed at the same time. Thus oil of garlic, C^6H^5S, is converted into oxide of allyl, C^6H^5O.

Formic acid, with the aid of heat, reduces mercury from *mercuric oxide*, also from mercuroso-mercuric or mercuric nitrate, and throws down calomel from solution of corrosive sublimate. Oxalate of ammonia likewise reduces corrosive sublimate to calomel. Gallic acid separates the metal from mercuric oxide and mercurous nitrate. Recently precipitated mercuric oxide yields with alcohol, metallic mercury and acetic acid. Volatile oils separate metallic mercury from mercurous nitrate and calomel from corrosive sublimate, being themselves more or less converted into resins. A solution of sugar at a boiling heat, converts mercuric oxide or acetate, into mercurous oxide or acetate, corrosive sublimate into calomel, and precipitates the metal from mercurous nitrate.

An aqueous solution of mercurous and mercuric nitrate together, reddens many substances rich in nitrogen, though this effect is not produced by either of these salts alone. Gelatin, the cellular tissue of the bones, serous, mucous, and fibrous membranes, albumen, either liquid or dried, cerebral substance, fibrin, casein (and therefore also milk), emulsin (and therefore also almonds), gluten (and therefore also flour), animal mucus, horn, nails, wool, and silk, moistened or mixed with solution of mercuroso-mercuric oxide, exhibit in ten seconds a faint, gradually increasing reddening, which, at temperatures between 40° and 60°, deepens into carmine and amaranth. This colouring serves as an indication of the presence of these substances in others, *e. g.*, of gluten in wheat-starch. [The purple colour changing to black when exposed to light, which is imparted to the fingers by solution of nitrate of mercury, has long been known.] Quinine, cinchonine, picromel, and uric acid, and likewise cholesterin, which contains no nitrogen, are coloured yellow by the mercuroso-mercuric solution. Morphine and narcotine assume at first a yellow colour, which afterwards turns brown. Non-azotized substances (with the exception of cholesterin), also cystic oxide, allantoin, osmazome, and urea, which contain nitrogen, exhibit no colouring. (Lassaigne & Lebaïllif, *Ann. Chim. Phys.* 45, 435; also *J. chim. méd.* 7, 102.)

Cupric oxide is reduced from its salts, most readily by certain kinds

of sugar, sometimes to cuprous oxide, sometimes to the metallic state (comp. V. 410).

Many organic compounds reduce *ferric* salts dissolved in water to ferrous salts.

Alcohol, oil of turpentine, sugar, gum, and paper effect this reduction only at a boiling heat, and then but imperfectly. Grass, hay, sawdust, and slips of wood, produce it in the cold, and completely in about three days. Peat and charcoal produce it in 24 hours, at medium temperatures, and in one or two hours at a boiling heat. (Stenhouse, *Phil. Mag. J.* 25, 199; also *Ann. Pharm.* 51, 284.)

Certain sulphur-compounds, such as the oils of garlic and mustard, are converted by *peroxide of lead* into oxygen-compounds, sulphide of lead being formed at the same time.

16. *Decompositions by Fixed Alkalis.*

The alkalis act chiefly by their predisposing affinity for acids, whereby they convert non-acid substances into acids, and weak acids into others of more powerfully acid character. If the action takes place at a high temperature, carbonic acid is formed, together with such organic acids as are most capable, when in combination with an alkali, of withstanding the effect of heat. On hydrocarbons the alkalis exert little or no action, even at high temperatures, probably because those bodies contain no oxygen.

A. Alkalis dispose organic compounds to take up oxygen from the air, thereby forming organic acids, carbonic acid, and other products. In this manner, many compounds which are permanent in the air when alone, are decomposed when exposed to the air in contact with an alkali.

When alcohol, containing potash in solution, is exposed to the air, acetic and formic acids are formed together with a brown resinous substance. Gallic, pyrogallic, and ellagic acid, dissolved in an aqueous alkali, exhibit, when exposed to the air, a varied succession of colours, till they are ultimately converted into a substance resembling humic acid. Many empyreumatic oils quickly turn brown in the air when potash is added to them.—Hæmatoxylin, the colouring matter of logwood, of violets, of hackled hemp, of gall, and of blood, and likewise albumen, which would keep for a long time in the air if dissolved in water *per se*, are quickly decomposed on the addition of potash. (Chevreul, *Mém. du Mus.* 1825, 367; also *Pogg.* 17, 176.)

B. Out of contact of air, the fixed alkalis give rise to the following decompositions, the action being often assisted by the presence of water.

a. Decomposition or splitting of the organic compound.

a. A neutral compound parts with hydrogen and oxygen in equal numbers of atoms, and is converted into an acid.

An aqueous solution of grape sugar, $C^{24}H^{24}O^{24}$ (or $C^{12}H^{12}O^{12}$), in which hydrate of lime has been dissolved, is converted, when set aside for some weeks in a close vessel, into kalisaccharic acid, $C^{24}H^{16}O^{16}$ (or $C^{12}H^{8}O^{8}$), and on heating the liquid, this compound is converted into a brown acid

($=C^{24}H^{8}O^{8}$ or $C^{12}H^{4}O^{4}$). (Péligot.) [According to the nucleus-theory, we must suppose that in this reaction, a portion of the oxygen originally contained within the nucleus passes to the outside.]

β. Or it is converted into an acid by taking up 2 At. hydrogen and 2 At. oxygen.

Isatin, $C^{16}H^{5}NO^{4}$, boiled with aqueous potash, is converted into isatinic acid, $C^{16}H^{7}NO^{6}$. Common camphor, $C^{20}H^{12}O^{2}$, passed in the state of vapour, under increased pressure in a closed tube, over a mixture of potash-hydrate and lime heated to 400°, produces campholate of potash, $C^{20}H^{17}KO^{4}$ (campholic acid$=C^{20}H^{18}O^{4}$).—Benzoyl, boiled with alcoholic potash, forms benzoylic acid, $C^{28}H^{12}O^{6}$, which unites with the potash. Anemonin, $C^{20}H^{12}O^{12}$, is converted by boiling with aqueous potash into anemonic acid, $C^{20}H^{14}O^{14}$; and cumarin, $C^{18}H^{6}O^{4}$, into cumaric acid, $C^{18}H^{8}O^{6}$.

γ. It is converted into an acid by taking up 2 At. oxygen from the alkaline hydrate, and giving off 2 At. hydrogen.

This transformation is sometimes effected by means of hydrate of potash in a state of fusion, the organic compound being gradually added to it,—sometimes by means of potash-lime, or soda-lime (*i. e.*, an intimate mixture of equal parts of burnt lime and hydrate of potash or soda, freed by ignition from excess of water), which is moistened with the liquid organic substance, and then gently heated. Most aldides when thus treated, are converted into monobasic acids belonging to the same series. When oil of bitter almonds is mixed with hydrate of potash in the state of fusion, benzoate of potash is formed, and 2 At. hydrogen are given off:

$$C^{14}H^{6}O^{2} + KO,HO = C^{14}H^{5}KO^{4} + 2H.$$

Oil of cinnamon yields cinnamate of potash:

$$C^{18}H^{8}O^{2} + KO,HO = C^{18}H^{7}KO^{4} + 2H.$$

Salicylous acid yields salicylate of potash:

$$C^{14}H^{6}O^{4} + KO,HO = C^{14}H^{5}KO^{6} + 2H.$$

Cuminol yields cuminate of potash:

$$C^{20}H^{12}O^{2} + KO,HO = C^{20}H^{11}KO^{4} + 2H.$$

If in these formulæ of the potash-salts, we substitute 1H for 1K, we obtain the formulæ of the free acids.

δ. The neutral compound may likewise be converted into an acid by taking up 2 At. oxygen, while 4 At. hydrogen are evolved, 2 At. of which belong to the compound itself.

This reaction is exhibited by the alcohols, when treated in the manner just described for the aldides. Wood-spirit, $C^{2}H^{4}O^{2}$, and hydrate of potash, KO,HO, produce formiate of potash with evolution of 4H. Similarly alcohol yields acetate of potash:

$$C^{4}H^{6}O^{2} + KO,HO = C^{4}H^{3}KO^{4} + 4H.$$

Fusel-oil yields valerate of potash:

$$C^{10}H^{12}O^{2} + KO,HO = C^{10}H^{9}KO^{4} + 4H.$$

Saligenin yields salicylate of potash:

$$C^{14}H^{8}O^{4} + KO,HO = C^{14}H^{5}KO^{6} + 4H.$$

Ethal yields ethalate of potash:

$$C^{32}H^{34}O^2 + KO,HO = C^{32}H^{31}KO^4 + 4H.$$

(*comp.* Dumas & Stas, *Ann. Chim. Phys.* 73, 103.)—For further observations on this point, *vid. Methylic ether.*

b. Decomposition attended with division of the organic compound.

a. Formation of an acid compound which unites with the alkali, and of a non-acid compound.

Chloral, treated with aqueous potash, yields chloroform and formiate of potash:

$$C^4HCl^3O^2 + HO + KO = C^2HKO^4 + C^2HCl^3.$$

β. Formation of two organic acids from a neutral and an acid organic compound.

When certain organic acids, containing a considerable number of carbon-atoms, are fused at a temperature near 200°, with about four times their weight of hydrate of potash, they are resolved, without any blackening, into two acids containing a smaller number of carbon-atoms. These two acids, so far as is yet known, are always oxalic and acetic acid, perhaps because their compounds with fixed alkalis are more capable than the salts of any other organic acid, of bearing a strong heat without decomposition. In these reactions the atoms of the original acid are sometimes sufficient to form the two new acids; sometimes, on the contrary, the requisite quantity of oxygen is made up from the water contained in the hydrate of potash, the hydrogen previously united with it escaping in the form of gas; sometimes again the hydrogen and oxygen of the water enter the new compound in equal numbers of atoms. In this manner, tartaric acid is resolved into 1 At. acetic and 1 At. oxalic acid:

$$C^8H^6O^{12} = C^4H^4O^4 + C^4H^2O^8.$$

Mucic acid yields 2 At. acetic and 1 At. oxalic acid:

$$C^{12}H^{10}O^{16} = C^8H^8O^8 + C^4H^2O^8.$$

Malic acid takes up 2 At. oxygen, and is converted into 1 At. acetic and 1 At. oxalic acid:

$$C^8H^6O^{10} + O^2 = C^4H^4O^4 + C^4H^2O^8.$$

Citric acid takes up H^2O^2, and is converted into 2 At. acetic and 1 At. oxalic acid:

$$C^{12}H^8O^{14} + H^2O^2 = C^8H^8O^8 + C^4H^2O^8.$$

Succinic acid takes up O^4 and yields 1 At. acetic and 1 At. oxalic acid:

$$C^8H^8O^8 + O^4 = C^4H^4O^4 + C^4H^2O^8.$$

Many non-acid compounds also, when mixed with four or five times their weight of hydrate of potash and a small quantity of water, and raised to a temperature far below redness, rapidly give off hydrogen, and consequently swell up strongly, and yield, without any blackening, a residue chiefly consisting of oxalate of potash.

Such is the case with common sugar, milk-sugar, gum-arabic, starch, cotton, sawdust; also with silk, glue, and uric acid, which, however, evolve ammonia as well as hydrogen, and leave carbonate of potash and cyanide of potassium as well as oxalate of potash. Hydrate of soda

acts like potash; carbonate of potash with tartaric acid, and carbonate of lime with starch do not yield oxalic acid. If the heat be continued and gradually raised, the whole of the oxalate of potash produced in these reactions is converted into carbonate. (Gay-Lussac, *Ann. Chim. Phys.* 41, 389; also *Pogg.* 17, 171.—*J. chim. méd.* 6, 20; also *Pogg.* 17, 528.)—*Semen Lycopodii* and indigo, fused with hydrate of potash, likewise yield acetic acid but no oxalic. (Muspratt, *Ann. Pharm.* 51, 271 and 280.)

Since sugar, gum, starch, and lignin, may be regarded as $x \,.\, C^4H^4O^4$ (the H and O which are deficient in some of these compounds, are supplied from the water of the hydrate of potash), the formation of the oxalic acid is most readily explained by supposing that xH^8 are evolved, and xO^4 enter from the water, so that $xC^4H^2O^8$ are produced. The formation of acetic acid, $C^4H^4O^4$, is still more easily explained; *e. g.*, cane-sugar, $C^{24}H^{22}O^{22}$, requires only the addition of 2HO to convert it into $6 \,.\, C^4H^4O^4$.

When hydrate of potash in small quantity acts upon sugar, &c., humic acid is formed as well as oxalic and acetic acid.

When 1 part of cane-sugar is added to the boiling concentrated solution of 3 pts. hydrate of potash, hydrogen gas is rapidly evolved, and compounds are formed of the potash with carbonic, formic, oxalic, acetic, and propionic acid, $C^6H^6O^4$. In this reaction, the heat is less, because more water is present. In the first instance, perhaps, the only products are carbonic, acetic, and propionic acid:

$$C^{24}H^{22}O^{22} + 4O = 2HO + 4CO^2 + 2C^4H^4O^4 + 2C^6H^6O^4.$$

But by the action of stronger heat in particular parts of the mixture, formic acid and oxalic acid are also produced.

γ. Two atoms of an acid give off 2 At. water and 2 At. carbonic acid, and are converted into a volatile neutral compound (a ketone).

Many compounds of a monobasic acid with a fixed alkali, in equal numbers of atoms, are resolved by dry distillation into a residue of alkaline carbonate and a distillate of ketone. Thus, 2 At. acetic acid and 2 At. baryta, yield, after thorough drying, 2 At. dry acetate of baryta, with evolution of 2 At. water:

$$2C^4H^4O^4 + 2BaO = 2C^4H^3BaO^4 + 2HO;$$

and these two atoms of baryta-salt are resolved, at a red heat, into 2 At. carbonate of baryta and 1 At. acetone;

$$2C^4H^3BaO^4 = 2(BaO,CO^2) + C^6H^6O^2.$$

Similarly, for the other ketones, as shown by the following conspectus:

2 Atoms.	C	H	O			C	H	O	Ketones.
Acetic acid	= 8	8	8	$-2CO^2$	$-2HO$ =	6	6	2	Acetone
Propionic acid	= 12	12	8	,,	,, =	10	10	2	Proprione
Butyric acid	= 16	16	8	,,	,, =	14	14	2	Butyrone
Valerianic acid	= 20	20	8	,,	,, =	18	18	2	Valerone
Benzoic acid	= 28	12	8	,,	,, =	26	10	2	Benzone
Campholic acid	= 40	36	8	,,	,, =	34	34	2	Campholone
Margaric acid	= 68	68	8	,,	,, =	66	66	2	Margarone

¶ By heating together the potash or soda salts of different monobasic acids, ketones of intermediate composition may be obtained; thus a mixture of acetate of soda and valerate of potash in equivalent propor-

tions, yields, when heated, a liquid having all the properties of a ketone, and the composition $C^{12}H^{12}O^2$:

$$C^4(H^2Na)O^4 + C^{10}(H^9K)O^4 = NaO,CO^2 + KO,CO^2 + C^{12}H^{12}O^2.$$

This substance is evidently intermediate in composition between acetone and valerone:

$$C^6H^6O^2 + C^{12}H^{12}O^2 = 2(C^{12}H^{12}O^2).$$

(Williamson, *Chem. Soc. Qu. J.* 4, 234; *vid. Ketones.*) ¶

δ. One atom of an acid strongly heated with a great excess of dry fixed alkali, is resolved in 2 At. carbonic acid and either hydrogen or a volatile, neutral organic compound.—Baryta and lime are best adapted for this purpose, inasmuch as they can be most readily obtained in the anhydrous state.

Thus the following transformations are produced, with loss of $2CO^2$.

	C	H	O		C	H
Formic acid	= 2	2	4	into Hydrogen gas =		2
Acetic acid	= 4	4	4	into Marsh gas =	2	4
Benzoic acid	= 14	6	4	into Benzol =	12	6
Cinnamic acid	= 18	8	4	into Cinnamene =	16	8
Cuminic acid	= 20	12	4	into Cumene =	18	12
Anthranilic acid	= $C^{12}H^7NO^4$			into Aniline =	$C^{12}H^7N$	
Nitrobenzoic acid	= $C^{14}H^5NO^8$			into Nitrobenzol =	$C^{12}H^5NO^4 = C^{12}H^5X$.	

In these reactions, a hydrocarbon is always formed containing C^2 less than the acid, and therefore placed one degree lower in the scale. Thus acetic acid, which belongs to the series of ethylene, C^4H^4, yields marsh-gas, C^2H^2, belonging to the series of methylene, C^2H^2, &c. Formic acid, alone, which itself belongs to the lowest order and contains only 2C, which is entirely expended in the formation of carbonic acid, $2CO^2$, cannot yield any hydrocarbon, but only 2H in the free state.

Also nitrotoluidine, $C^{14}H^7X = C^{14}H^7NO^4$, which is isomeric with anthranilic acid, is resolved, by passing it in the state of vapour over red-hot lime, into $2CO^2$ and aniline, $C^{12}H^7N$: But salicylamide, $C^{14}H^6AdO^2,O^2$, which is also metameric with anthranilic acid, yields, when thus treated, very little aniline, but chiefly ammonia and phenous acid, $C^{12}H^6O^2$. (Hofmann and Muspratt, *Ann. Pharm.* 53, 222.)

Just as, in the decomposition of anthranilic acid by fixed alkalis, a non-oxygenated alkaloid, viz., aniline, passes over, so likewise quinine, cinchonine, and strychnine yield another such alkaloid, viz., quinoline,—with these differences, however, viz., first, that, instead of an anhydrous alkali, hydrate of potash is required, so that its water may furnish oxygen for the carbonic acid; and secondly, that, besides the hydrogen of this water, hydrogen is likewise evolved from the quinine, &c., itself.

Those monobasic acids which contain 6 At. oxygen [two in the nucleus and four outside], likewise yield, when distilled with dry fixed alkalis, not 3 but only 2 At. carbonic acid, the remaining 2 At. oxygen remaining in the new compound which goes off in vapour.—Salicylic acid, $C^{14}H^6O^2,O^4$, distilled with excess of baryta, yields phenous acid, $C^{12}H^6,O^2$.—Anisic acid, $C^{16}H^8O^2,O^4$, yields anisol, $C^{14}H^8,O^2$. Even salicylate of methyl, $C^2H^3O,C^{14}H^6O^5$, which is metameric with anisic acid, yields the same compound, viz., anisol.

A similar decomposition, depending only on the formation of carbonic acid, is sometimes, though rarely, produced in the wet way.—Lecanorin,

$C^{16}H^8O^8$, boiled with baryta-water, yields carbonate of baryta, $2(BaO,CO^2)$, which is precipitated, and orcin, $C^{16}H^8O^4$.

Peculiar behaviour of Compounds containing Nitrogen or Chlorine towards Fixed Alkalis.

a. All azotized organic compounds, when treated with excess of aqueous fixed alkalis, in a manner adapted to their peculiar nature, give off all their nitrogen in the form of ammonia.

Compounds containing nitrogen in the form of amidogen, require but a slight heating with aqueous potash to separate all their nitrogen in the form of ammonia. For each atom of nitrogen which they contain, an atom of ammonia is evolved, and 2 At. water take its place; and in combination with the potash there remains an acid having the same composition as the amidogen-compound, excepting that $1O^2$ or $2O^2$ have been substituted for 1NH or 2NH; the acid likewise saturates a number of atoms of potash equal to the number of atoms of ammonia evolved.

Thus, oxamic acid, $C^4H^3NO^6$, treated with excess of aqueous potash, yields, with decomposition of 2HO, oxalic acid, $C^4H^2O^6$, and NH^3 (or since the product is not actually free oxalic acid, but oxalate of potash :

$$C^4H^3NO^6 + HO + KO = C^4HKO^8 + NH^3).$$

Oxamide, $C^4H^4N^2O^4$, is resolved, with decomposition of 4HO, into $C^4K^2O^8$ and $2NH^3$; or,

$$C^4H^4N^2O^4 + 2HO + 2KO = C^4K^2O^8 + 2NH^3.$$

Other compounds, which do not contain nitrogen in the form of amidogen—indigo and glycocol, for example—either give off no ammonia when boiled with aqueous potash, or yield it very slowly and in small quantity, so that, after several hours' boiling, there still remains a nitrogenous residue, such as gelatin, albumen, or fibrin.

But all azotized organic compounds, in whatever quantity and in whatever state the nitrogen may exist in them, give it off completely in the form of ammonia, when they are heated to redness with a sufficient excess of a mixture of hydrate of potash or soda and quicklime. (Berzelius, *J. pr .Chem.* 23, 231; Varrentrapp & Will, *Ann. Pharm.* 39, 265.)

In this reaction, the oxygen of the water in the hydrate of potash burns that portion of the carbon which does not escape in combination with hydrogen, and converts it wholly into carbonic acid; while the hydrogen of the water unites with the nitrogen and forms ammonia, if the organic compound, like cyanogen, mellon, and uric acid, does not contain within itself a quantity of hydrogen sufficient for that purpose. The rest of the hydrogen escapes, either in the gaseous form, as free hydrogen, marsh-gas, or olefiant-gas, or in the form of oily or camphoroidal hydrocarbons, such as benzin and naphthalin. On the first application of the heat, cyanide of potassium and cyanate of potash may be formed; but at a red heat, and in contact with a sufficient excess of hydrate of potash, these compounds are completely converted into ammonia and carbonic acid. (Varrentrapp & Will.)

Ammonia may be obtained even from a nitrate by ignition with potash-lime, provided that a non-azotized organic body be added to the

mixture; but it is only when the latter is present in very great excess that the whole of the nitrogen is given off in the form of ammonia. Thus, 1 pt. nitre with 2 sugar yields only 0·23 of the quantity of ammonia which should be formed if all the nitrogen of the nitric acid were converted into it; with 10 sugar, it yields 0·43, and with 40 sugar, 0·79 ammonia, which is not quite ¾ of the whole. (Varrentrapp & Will.)

On this entire conversion of the nitrogen of organic compounds into ammonia, is founded the process, first given by Varrentrapp & Will, for the determination of ammonia. Subsequently, Will showed (*Ann. Pharm.* 45, 95), that no ammonia is given off when non-azotized organic compounds are heated with pure soda-lime, contrary to the statement of Reiset (II., 419), who used in his experiments, as he afterwards found, soda which was contaminated with nitrate.

Many nitrogenous substances, ignited with dry alkalis, either caustic or carbonated, produce a metallic cyanide in the residue. The charcoal here reduces the alkali to the metallic state, and the reduced metal takes up two other atoms of carbon and 1 At. nitrogen in the form of cyanogen. The metallic cyanide is also formed when hydrate of potash is used; but if this substance is in excess, its water oxidizes the carbon of the cyanogen on further ignition, converting it into carbonic acid, and the nitrogen goes off in the form of ammonia.

b. Organic Compounds containing Chlorine are completely decomposed, with formation of metallic chloride, when their vapour is passed through a red-hot tube filled with lime. On the contrary, when boiled with aqueous alkalis, some of these compounds, such as $C^{12}H^3Cl^3$, remain undecomposed; others, such as $C^{12}H^6Cl^6$, lose a portion of their chlorine; others again, as C^4H^5Cl, give up the whole.

The alkali either abstracts hydrogen in the same number of atoms as chlorine, so that hydrochloric acid is in fact withdrawn, and a metallic chloride and water produced:

$$\underbrace{C^{12}H^6Cl^6}_{\text{Chlorobenzin.}} + 3KO = \underbrace{C^{12}H^3Cl^3}_{\text{Chlorobenzide.}} + 3KCl + 3HO.$$

$$\underbrace{C^4H^4Cl^2}_{\text{Oil of olefiant gas.}} + KO = \underbrace{C^4H^3Cl}_{\text{Chloride of acetyl.}} + KCl + HO.$$

Or the abstracted chlorine is replaced by the O of the alkali, and moreover, H and O from the water present enter the compound.—An example of this mode of action is seen in the transformation of hydrochloric ether by potash into alcohol and chloride of calcium:

$$C^4H^5Cl + KO + HO = C^4H^6O^2 + KCl.$$

Or, in place of the abstracted chlorine, an equal number of atoms of oxygen from the alkali enters the compound, and then also an atom of the alkali itself. Chloro-benzoyl, treated with potash, yields benzoate of potash and chloride of potassium:

$$C^{14}H^5ClO^2 + 2KO^2 = C^{14}H^5KO^4 + KCl.$$

Chloroform heated with aqueous potash in a closed tube to a temperature above 100°, yields formiate of potash and chloride of potassium:

$$C^2HCl^3 + 4KO = C^2HKO^4 + 3KCl.$$

Iodine- and bromine-compounds exhibit similar relations towards fixed alkalis.

Many *copulated compounds* are decomposed by aqueous alkalis, into an acid constituent which unites with the alkali, and a non-acid portion which is separated: *e. g.*, Compound Ethers, Fats, &c.

17. *Decompositions by Ammonia.*

Many organic compounds, both acid and non-acid, when treated under certain circumstances with ammonia, form with it peculiar nitrogenized compounds, which, for the most part, are denominated *Amidogen-compounds*, or *Amides;* the action is attended with separation of water (or of hydrochloric or hydrobromic acid, if the organic compound contains iodine or bromine).—In some cases, it is sufficient to leave the organic compound for a while in contact with ammoniacal gas, or with aqueous or alcoholic ammonia; *e. g.*, Oil of Bitter-almonds, Chlorobenzoyl, Furfurol.—In other cases, the neutral or acid ammonia-salt of an organic acid is strongly heated.—In other cases, again, the acid upon which the ammoniacal gas or its solution in absolute alcohol is to work, is converted into an anhydride, which then, on being subjected to the action of ammonia, either gives up no water, as is the case with Lactide, or a smaller number of atoms of water, as is the case with Succinic anhydride.—Or a compound ether (of the third class) formed with an acid and alcohol or wood-spirit, is brought in contact with ammonia; the alcohol is then reproduced, and an amidogen-compound formed.—In this manner, Oxalic ether yields Oxamide:

$$2C^4H^5O,C^4O^6 + 2NH^3 = 2C^4H^6O^2 + C^4H^4N^2O^4.$$

Succinic ether yields Succinamide:

$$2C^4H^5O,C^8H^4O^6 + 2NH^3 = 2C^4H^6O^2 + C^8H^8N^2O^4.$$

The compounds thus formed are sometimes acid (amidogen-acids), sometimes neutral, sometimes basic; the last-mentioned compounds constitute a large proportion of the artificial alkaloids.

According to the nature of the organic compound, and the number of atoms of that compound, and of ammonia which act upon each other, and the number of atoms of water separated, the following cases may be distinguished.

a. One atom of an aldide (understanding generally by that term, those bodies which may be regarded as compounds of a primary or secondary nucleus with 2O) takes up 1 At. ammonia, and forms therewith (2 At. water being separated) either a nitrogen-nucleus (containing N as such) + 2H outside, or an amidogen-nucleus (*i. e.*, a nucleus in which part of the hydrogen may be considered as replaced by amidogen = NH^2). In this case 2O are replaced by NH.

In this manner, the following transformations are produced: Phenous acid into aniline:

$$C^{12}H^6,O^2 + NH^3 - 2HO = C^{12}H^7N = C^{12}H^5N,H^2\ (= C^{12}H^5Ad);$$

Benzil into Imabenzile:

$$C^{28}H^{10}O^4\ (= C^{26}H^{10}O^2,O^2) + NH^3 - 2HO = C^{26}H^{11}NO^2\ (= C^{26}H^9Ad,O^2);$$

Isatin into Imesatin:

$$C^{16}H^5NO^4\ (= C^{16}H^5NO^2,O^2) + NH^3 - 2HO = C^{16}H^6N^2,O^2\ (= C^{16}H^4AdN,O^2).$$

(The formulæ in brackets are expressed according to Laurent's view, the nucleus to the left of the comma, the enveloping atoms to the right.)

b. 1 At. of a monobasic acid (containing 4 At. oxygen outside the nucleus) likewise takes up 1 At. ammonia, separates 2 At. of water, and is thereby converted into a compound of an amidogen-nucleus with 2 At. oxygen (*e. g.*, an amidogen-aldide). In this case also 2 At. O are replaced by NH.

Chloracetic acid is converted (when chloracetic ether is treated with ammonia) into chloracetamide:

$$C^4HCl^3,O^4 + NH^3 - 2HO = C^4H^2Cl^3NO^2 \; (= C^4AdCl^3,O^2);$$

Lactic acid (used in the form of lactide) is converted into Lactamide:

$$C^6H^6O^6 \; (= C^6H^6O^3,O^4) + NH^3 - 2HO = C^6H^7NO^4 \; (= C^6H^5AdO^2,O^2);$$

Butyric acid (by treating butyric ether with ammonia) into Butyramide:

$$C^8H^8,O^4 + NH^3 - 2HO = C^8H^9NO^2 \; (= C^8H^7Ad,O^2);$$

Salicylic acid (by heating salicylate of ammonia) into Salicylamide:

$$C^{14}H^6O^6 \; (= C^{14}H^6O^2,O^4) + NH^3 - 2HO = C^{14}H^7NO^4 \; (= C^{14}H^5AdO^2,O^2);$$

Indigotic acid (by treating indigotate of methyl with ammonia) into Anilamide:

$$C^{14}H^5NO^{12} \; (= C^{14}H^5XO^2,O^4) + NH^3 - 2HO = C^{14}H^6N^2O^8 \; (= C^{14}H^4AdXO^2,O^2);$$

Chloranilam into Chloranilamide:

$$C^{12}H^3Cl^2NO^6 \; (= C^{12}HAdCl^2O^2,O^4) + NH^3 - 2HO = C^{12}H^4Cl^2N^2O \; (= C^{12}Ad^2Cl^2O^2,O^2).$$

c. One At. of a bibasic acid (containing 6 At. oxygen outside the nucleus) with 2 At. ammonia, yields 4 At. water, and forms an amidogen-aldide (*i. e.*, a substance which may be regarded as a compound of an amidogen-nucleus with 2 At. oxygen). In that case, 4O are replaced by 2NH.

Thus, under certain circumstances: Oxalic acid is converted into Oxamide:

$$C^4H^2O^8 \; (= C^4H^2O^2,O^6) + 2NH^3 - 4HO = C^4H^4N^2O^4 \; (= C^4Ad^2O^2,O^2);$$

Fumaric acid into Fumaramide:

$$C^8H^4O^8 \; (= C^8H^4O^2,O^6) + 2NH^3 - 4HO = C^8H^6N^2O^4 \; (= C^4H^2Ad^2O^2,O^2);$$

Succinic acid into Succinamide:

$$C^8H^6O^8 \; (= C^8H^6O^2,O^6) + 2NH^3 - 4HO = C^8H^8N^2O^4 \; (= C^8H^4Ad^2O^2,O^2);$$

Pyromucic acid into Pyromucamide:

$$C^{10}H^4,O^6 + 2NH^3 - 4HO = C^{10}H^6N^2O^2 \; (= C^{10}H^2Ad^2,O^2);$$

Mucic acid into Mucamide:

$$C^{12}H^{10}O^{16} \; (= C^{12}H^{10}O^{10},O^6) + 2NH^3 - 4HO = C^{12}H^{12}N^2O^{12} \; (= C^{12}H^8Ad^2O^{10},O^2);$$

Camphoric acid into Camphoramide:

$$C^{20}H^{16}O^8 \; (= C^{20}H^{16}O^2,O^6) + 2NH^3 - 4HO = C^{20}H^{16}N^2,O^4 \; (= C^{20}H^{14}Ad^2O^2,O^2).$$

d. 1 At. of a bibasic acid with 1 At. ammonia forms a monobasic acid, with elimination of only 2 At. water. Here 2O are replaced by NH.

In this manner, Oxalic acid is converted into Oxamic acid:

$$C^4H^2O^8 \; (= C^4H^2O^2,O^6) + NH^3 - 2HO = C^4H^3NO^6 \; (= C^4HAdO^2,O^4).$$

e. 2 At. of a monobasic acid with 1 At. ammonia yield 4 At. water, and form an amidogen-aldide, whose nucleus contains twice as many atoms of carbon and of the other substances in the nucleus, as the nucleus of the acid. In this case, 4O and 1H are replaced by only 1N.

Thus; 2 At. Benzoic acid are converted into Benzimide:

$$2(C^{14}H^{6},O^{4}) + NH^{3} - 4HO = C^{28}H^{11}NO^{4} \; (= C^{28}H^{9}AdO^{2},O^{2}).$$

Similarly, 2 At. Opianic acid into Opiammon:

$$2C^{20}H^{10}O^{10} \; (= C^{20}H^{10}O^{6},O^{4}) + NH^{3} - 4HO = C^{40}H^{19}NO^{16} \; (= C^{40}H^{17}AdO^{14},O^{2}).$$

f. 1 At. of a bibasic acid with 1 At. ammonia forms an amidogen-nucleus, with separation of 4 At. water. Here 4O and 1H are replaced by 1N.

Succinic acid is thereby converted into Bisuccinamide:

$$C^{8}H^{6}O^{8} \; (= C^{8}H^{6}O^{2},O^{6}) + NH^{3} - 4HO = C^{8}H^{5}NO^{4} \; (= C^{8}H^{3}Ad,O^{4});$$

Phthalic acid into Phthalimide:

$$C^{16}H^{6}O^{8} \; (= C^{16}H^{6}O^{2},O^{6}) + NH^{3} - 4HO = C^{16}H^{5}NO^{4} \; (= C^{16}H^{3}AdO^{4});$$

Mellitic acid into Paramide:

$$C^{8}H^{2}O^{8} \; (= C^{8}H^{2}O^{2},O^{6}) + NH^{3} - 4HO = C^{8}HNO^{4}.$$

In this last case, the quantity of hydrogen is too small by 1 At. to admit the assumption that paramide contains amidogen; this circumstance, therefore, is unfavourable to the amidogen-theory.

g. 1 At. of a monobasic acid takes up 1 At. ammonia, yielding 4 At. water, and forming a cyanogen-compound.

Thus, Formic acid is converted into Hydrocyanic acid:

$$C^{2}H^{2}O^{4} + NH^{3} - 4HO = C^{2}NH.$$

h. 3 At. of an aldide, by taking up 2 At. ammonia, form 2 At. water, and are transformed into a substance which may be regarded as a compound of 2 At. nitrogen or hydrogen with a nucleus which is three times as great as that of the original aldide. In this case, 6O are replaced by 2N.

Furfurol, $C^{10}H^{4}O^{4}$ ($=C^{10}H^{4}O^{3},O$; therefore nucleus $= 10 : 6$) is first converted into Furfuramide; and this compound, when boiled with water, is again resolved into ammonia and furfurol, but by boiling with potash, is immediately converted into Furfurine, an alkaloid isomeric with furfuramide:

$$3C^{10}H^{4}O^{4} + 2NH^{3} - 6HO = C^{30}H^{12}N^{2}O^{6} \text{ (nucleus} = 30 : 18).$$

Bitter almond oil yields Benzhydramide, Hydrobenzamide, Amarine (an alkaloid), and other isomeric compounds:

$$3(C^{14}H^{6},O^{2}) + 2NH^{3} - 6HO = C^{42}H^{18}N^{2}.$$

In a similar manner, Cinnamon oil yields *Hydrure d'azocinnamyle:*

$$3(C^{18}H^{8},O^{2}) + 2NH^{3} - 6HO = C^{54}H^{24}N^{2}.$$

Salicylous acid, $C^{14}H^{6}O^{4}$ ($=C^{14}H^{6}O^{3},O^{2}$; nucleus $= 14 : 8$), yields Salicylimide:

$$3C^{14}H^{6}O^{4} + 2NH^{3} - 6HO = C^{42}H^{18}O^{6}N^{2} \text{ (nucleus} = 42 : 24).$$

Similarly, Chlorosalicyl yields Chlorosamide:

$$3C^{14}H^{5}ClO^{4} \; (= C^{14}H^{5}ClO^{2},O^{2}) + 2NH^{3} - 6HO = C^{42}H^{15}Cl^{3}N^{2}O^{6} \; (= C^{42}H^{15}Cl^{3}O^{6},N^{2}).$$

Hydranisyl, $C^{16}H^8O^4$ ($=C^{16}H^8O^2,O^2$; nucleus $= 16:10$) yields Anishydramide:

$$3C^{16}H^8O^4 + 2NH^3 - 6HO = C^{48}H^{34}O^6N^2 \text{ (nucleus} = 48:30).$$

In all these cases, a compound is formed containing three times as many carbon-atoms as the original compound, inasmuch as 3 At. of the same are held together by 2 At. nitrogen (apparent increase of the number of carbon-atoms (p. 43).—Bineau (*Ann. Chim. Phys.* 67, 242) proposes to reduce the atomic weight of nitrogen to $\frac{1}{3}$ of its ordinary amount ($=\frac{14}{3}$, according to the numbers of this Hand-book), in order to obtain more simple relations; *e.g.*, instead of $C^{48}H^{16}N^2$, we should have $C^{16}H^8N^2$.

i. 1 At. of an aldide whose nucleus contains chlorine forms with 1 At. ammonia, 1 At. of an aldide whose nucleus contains amidogen, the action being attended with separation of 1 At. hydrochloric acid. In this case, 1Cl is replaced by NH^2.

Chlorobenzoyl is converted into Benzamide:

$$C^{14}H^5Cl,O^2 + NH^3 - HCl = C^{14}H^7NO^2 \ (= C^{14}H^5Ad,O^2).$$

Of similar nature is the conversion of Chloroxycarbonic ether into Urethane:

$$C^5H^5ClO^4 + NH^3 - HCl = C^5H^7NO^4.$$

Most of the compounds produced by ammonia may be reconverted, in presence of water, into ammonia and the organic substance from which they were formed, resuming, in fact, the oxygen and hydrogen which in their formation had been separated in the form of water. This transformation may take place under the following circumstances.

1. Heating with water. For this purpose, boiling with water under the ordinary atmospheric pressure is often sufficient: *e.g.*, Oxamic acid, Benzamide, Hydrobenzamide, Paramide, Phthalimide, Furfuramide. But it is often necessary and always more expeditious to inclose the substance together with water in a sealed tube, and heat it to a temperature between 150° and 220°: *e.g.*, Oxamide, Euchronic acid, Lactamide, Mucamide, Opiammon.

2. Addition of an aqueous acid, whose affinity for ammonia, especially on the application of heat, favours the production of that substance: Oxamide, Bisuccinamide, Benzamide, Salicylamide, Furfuramide, Lactamide, Chloranilam. In the case of Opiammon, oil of vitriol is alone capable of affecting this transformation, and acts even in the cold; whereas dilute sulphuric acid has no action upon it, even when heated.

3. Addition of the stronger fixed bases, especially of potash, in case the amidogen-compound has been formed from ammonia and an acid. The fixed alkali acts by virtue of its predisposing affinity for the acid, the ammonia being thereby set free. Cold aqueous potash acts in this manner only on Chloranilam. Boiling potash-solution induces the transformation of Chloracetamide, Fumaramide, Bisuccinamide, Lactamide, Butyramide, Anilamide, Chloranilam, Chloranilamide, Benzimide, Benzamide, Salicylamide, Salicylimide, Phthalimide.—Benzimide is not decomposed by boiling with aqueous potash; but on heating it with hydrate of potash moistened with alcohol, the decomposition takes place. Asparagine heated with salifiable bases and with water, gives off half its nitrogen in the form of ammonia, and then remains in combination with the base in the form of aspartic acid.—Opiammon, which may be decomposed by heating with water, resists the action of boiling potash.—

Furfuramide, which, when boiled with water or treated with acids, is resolved into ammonia and furfurol, is converted by contact with potash into Furfurine, an alkaloid isomeric with furfuramide itself, and not decomposible by boiling potash.

But many of the compounds produced by ammonia cannot, by any of the above-mentioned processes, be reconverted into ammonia and the original substance. Such is the case with Aniline, Benzilam, $C^{26}H^9N$, and Amarine.

There are four states in which the nitrogen of the ammonia may be supposed to enter these compounds; viz., as Ammonia, NH^3; as Amidogen, NH^2; as a double atom of Laurent's Imidogen, viz., as NH; or as Nitrogen in its proper form. In the first case, all the water which is eliminated must be supposed to proceed from the hydrogen and oxygen of the original organic compound; in the other cases, it is sometimes wholly, sometimes partly, produced from the hydrogen of the ammonia.

These compounds rarely contain nitrogen in the form of ammonia, with perhaps the single exception of chloranilam, this being, in fact, the only one among them which evolves ammonia when treated with *cold* aqueous potash.—A single atom of imidogen, as Laurent considers it, viz., N^1H^1, cannot be supposed to exist in them, at least according to the atomic weights adopted in this Hand-book, half-atoms being inadmissible. The assumption of a double atom of imidogen, NH, would introduce uneven numbers of atoms, and is therefore improbable. If, for example, Butyramide, $C^8H^9NO^2$, were thus considered, we should have $C^8H^8ImO^2$, that is to say, 19 atoms; in Paranide, $C^8HNO^4=C^8ImO^4$, the number of atoms would be 13, and similarly in all other cases. In certain compounds, however, the supposition of 2NH is admissible.

The choice then lies, for the most part, between nitrogen in its own proper form and amidogen. Probably some compounds contain it in the one, some in the other state. We may suppose that those compounds which can be reconverted into ammonia and the original compound contain amidogen, and the rest contain nitrogen in its proper form; *e. g.*, Aniline, Imabenzil, Benzilam, and Amarine.

In the cases mentioned in *h* (p. 142), $2NH^3$ are taken up and 5HO separated. The simplest supposition that can be made in such cases is that the 6H of the $2NH^3$ are expended in the formation of the 6HO, and the 2N remain as such in the product. If, however, we remember that furfurol, when treated with ammonia, is first converted into furfuramide, which again is decomposed by water and acids into ammonia and furfurol, and converted by contact with potash into the isomeric body, furfurine,—moreover, that most of the products described in *h* (p. 142) are capable of reconversion,—it will appear probable, even in these cases, that the 2N of the compound are originally present as $2NH^2$ or 2NH, but that under certain circumstances, the conversion of furfuramide into furfurine, for example, the 2N are freed from their state of combination with H^2.—Thus perhaps: Furfuramide$=C^{30}H^{10}(NH)^2O^6$, and Furfurine$=C^{30}H^{10}N^2O^6,H^2$ (nucleus=30 : 18). Similarly, Benzhydramide is perhaps $C^{42}H^{16}(NH)^2$; and Amarine, which is isomeric with it, is $C^{42}H^{16}N^2,H^2$ (nucleus=42 : 18).

In the mode of decomposition given in *i* (p. 143), $1NH^3$ probably gives up 1H to 1Cl, and NH^2 remains in the new compound.

In decompositions, according to *b* and *d*, 2HO are produced for $1NH^3$; and in those, according to *c*, 4HO to $2NH^3$.—In such cases, the simplest view is perhaps that of Gerhardt, viz., that since $1NH^3$ gives up 2H to form 2HO, or $2NH^3$ give up 4H to form 4HO, the new compound must contain

1 or 2NH. But it is likewise possible that $1NH^3$ gives up only 1H to 1O of the compound, being thereby reduced to NH^2, and that the second HO is formed merely from the latter. That this supposition is not improbable may be seen from the instances adduced in *e*, *f*, and *g*, in which 4HO are produced from $1NH^3$; so that we are obliged to assume a separation of at least 1HO from the organic compound itself.—If aniline, formed as in *a*, contains nitrogen as such, which is the more probable supposition, it follows that 2H must have separated in the form of 2HO from the NH^3, and the third H, separated from the N, must have entered the compound.

From all this it appears probable that compounds formed from ammonia, according to *b*, *c*, *d*, *e*, *f*, contain the nitrogen of the ammonia in the form of amidogen, NH^2, and are therefore true amidogen-compounds or amides; hence they are capable of reconversion. Paramide, C^8HNO^4, alone forms an exception, inasmuch as, from its composition, it cannot contain NH^2, but is nevertheless very easily reconverted into ammonia and mellitic acid. This fact requires further elucidation.

In the cases described in *h*, a compound appears to be formed containing 2NH, but sometimes capable of giving out 2H from the nucleus, and being converted into a compound which contains nitrogen in its own proper form.

It appears then that nitrogen may be contained in an organic compound in three or four different states, viz., as Nitrogen itself=N; as Hyponitric acid = NO^4; as Amidogen = NH^2; and perhaps also as Imidogen=NH.

18. *Decompositions and Transformations by Hydrosulphuric Acid.*

a. Hydrosulphuric acid gives up hydrogen to many compounds, with precipitation of sulphur. Thus it converts Chinone, $C^{12}H^4O^4$, into Hydrochinone, $C^{12}H^6O^4$; Isatine, $C^{16}H^5NO^4$, into Isatide, $C^{16}H^6NO^4$.

b. It abstracts the 4 At. oxygen from the NO^4 in nitro-compounds, and transfers to them 2 At. hydrogen, with precipitation of sulphur, thereby converting them into compounds which contain nitrogen in its proper form, or perhaps as amidogen (p. 75).

19. *Decompositions by Sulphide of Potassium.*

Sulphide of potassium decomposes many organic compounds by double affinity, yielding chloride of potassium and an organic sulphur-compound. Hydrochloric ether, C^4H^5Cl, with KS forms KCl and sulphide of ethyl, C^4H^5S; with KS,HS, it forms KCl and Mercaptan, $C^4H^6S^2$.

20. *Decompositions by the Alkali-metals.*

Potassium and sodium, even when heated, do not act upon compounds containing only carbon and hydrogen. When heated with compounds which contain large quantities of oxygen, they take up that element, producing combustion and carbonization, and forming a mixture of charcoal and an alkaline carbonate. Dry oxalic acid thus treated produces vivid combustion; tartaric and mucic acid, feeble combustion; with citric acid, carbonization takes place without combustion.

From liquid compounds comparatively poor in oxygen, potassium, at ordinary or slightly elevated temperatures, drives out part of the hydrogen with effervescence, and takes its place in the compound.

Thus, acetic acid, $C^4H^4O^4$, is converted into anhydrous acetate of potash, $C^4H^3KO^4$,—absolute alcohol, $C^4H^6O^2$, into the compound $C^4H^5KO^2$, —and cuminol, $C^{20}H^{12}O^2$, into the compound $C^{20}H^{11}KO^2$. On the addition of water, the original compound is reproduced, together with potash. A similar action is exerted by potassium on other alcoholic liquids, and upon volatile oils containing oxygen. The decomposition of oxalic ether by potassium is of a more complicated character.

Potassium heated with any nitrogenous organic compound, forms cyanide of potassium.

The detection of very small quantities of nitrogen is based upon this reaction. A piece of potassium is placed at the bottom of a narrow test-tube, and covered with the substance to be examined; the mixture is then heated to redness till the excess of potassium is volatilized; the residue dissolved in water; the solution precipitated by a ferroso-ferric salt, and mixed with excess of hydrochloric acid, which, if cyanide of potassium has been formed, leaves a residue of Prussian blue. Substances not containing nitrogen as such, likewise give this reaction if they contain nitric or nitrous acid. Hydrate or carbonate of potash, instead of potassium, does not give so delicate an indication of nitrogen. (Lassaigne, *J. chim. méd.* 19, 201; also *J. pr. Chem.* 20, 143.)

With the chlorine and bromine occurring in many organic compounds, potassium often forms chloride or bromide of potassium; in some cases, however, another portion of the potassium is transferred to the compound.

Thus hydrochloric ether, treated with potassium, gives off no gas, but forms a white mass, which is probably a mixture of chloride o potassium with the new potassium-compound:

$$C^4H^5Cl + 2K = C^4H^5K + KCl.$$

In other cases again the place of the abstracted atoms of chlorine is supplied partly by the potassium, and partly by hydrogen from water which may be present. Aqueous chloracetate of potash, in contact with potassium-amalgam, is converted into acetate of potash and chloride of potassium:

$$C^4Cl^3KO^4 + 6K + 3HO = C^4H^3KO^4 + 3KCl + 3KO.$$

21. *Decompositions and Transformations by Water.*

Water may transform an organic compound, by imparting to it hydrogen and oxygen in equal numbers of atoms.

a. The compound remains undecomposed, merely becoming richer in hydrogen and oxygen.—Lactide, $C^6H^4O^4$, is slowly converted by cold water, more quickly by hot water, into lactic acid, $C^6H^6O^6$. Similar transformations are exhibited by the acid anhydrides (*vid. Organic acids*). Oil of turpentine, $C^{20}H^{16}$, placed, under certain circumstances, in contact with water, forms the camphor or stearoptene of turpentine, $C^{20}H^{20}O^4$. Common sugar, $C^{12}H^{11}O^{11}$ (or $C^{24}H^{22}O^{22}$), is converted by water at 200° into grape-sugar, $C^{12}H^{12}O^{12}$ (or $C^{24}H^{24}O^{24}$).

b. Or the addition of hydrogen and oxygen from the water causes the original compound to resolve itself into several new compounds.—Oxamide, $C^4H^4N^2O^4$, heated to 226° with water in a sealed tube, takes up

4HO, and is resolved into oxalic acid, $C^4H^2O^8$ and $2NH^3$; similarly, oxamic acid, $C^4H^2NO^6$, even at 100°, takes up 2HO, and is converted into acid oxalate of ammonia; also asparagin, at 150°, into aspartic acid and ammonia.

V. Classification of Organic Compounds.

The classification which will be adopted in the present work, *so far as our present knowledge of organic compounds allows*, is based on the following principles.

It is supposed, in accordance with Laurent's views, that organic compounds consist, either of primary nuclei, or of secondary or derivative nuclei, or of compounds of these nuclei with various substances externally attached.

We begin, as in Laurent and Gerhardt's system, with the consideration of those nuclei which contain the smallest number of carbon-atoms, and thence proceed, in a gradually ascending scale, to those which contain the greatest number of carbon-atoms. It will be readily seen, that we thus proceed from the lowest to the highest grade of organic compounds.

When a nucleus or other organic substance may be probably supposed to be not simple but compound, that is to say, produced by the combination of two or more elementary nuclei, or other elementary organic substances, the place of that substance in the scale is determined, not according to the total number of its carbon-atoms, but according to the number of carbon-atoms in that one of its components which contains the largest number of those atoms.

When two primary nuclei contain the same number of carbon-atoms, but different numbers of hydrogen-atoms, such as Phenylene, $C^{12}H^6$, and Oleene, $C^{12}H^{12}$; or as Naphthene, $C^{20}H^8$, and Terebene, $C^{20}H^{16}$, the nucleus containing the smaller proportion of hydrogen will be considered before the other.

In connection with each primary nucleus, we shall consider, in the second place, its compounds with substances which attach themselves externally to it. These are especially, H or H^2; HO or H^2O^2; O^2, O^4 or O^6; HS or H^2S^2; S^2 or S^4; HI; I^2; HBr; Br^2, Br^4 or Br^6; HCl; Cl^2, Cl^4 or Cl^6.

In combinations of a nucleus with substances externally attached, the composition of the nucleus may generally be viewed in more ways than one. Is alcohol to be considered as C^4H^4,H^2O^2, and acetic acid as C^4H^4,O^4, or are these compounds respectively C^4H^3O,H^3O, and C^4H^3O,HO^3? Although for reasons already adduced (pp. 20, 21, and 32, 33), the latter view may be the more probable, still the question cannot be considered as definitely settled. The former view has been preferred in the classification, because it yields simpler formulæ, and the nucleus C^4H^4, for example, is known to exist in the separate state, whereas C^4H^3O is not. With regard, however, to certain substances, the formulæ founded on the latter theory will be given as the more correct; and then the former theory, so far as necessary, will be distinguished as *Th.* 1, the latter as *Th.* 2.

Since the nucleus is, as it were, enveloped by the atoms which attach

themselves to it, the latter may be distinguished from the atoms of the nucleus by the title of *Envelope-atoms* (*Hüllen-atome*); they form with the nucleus, compounds which may be called *Envelope-nuclei* (*Hüllen-Kerne*); and these consist of a *Nucleus* (*Kern*) and an *Envelope* (*Hülle*). The substances which form the nucleus are called *Nucleus-matters* (*Kern-stoffe*), and those which compose the envelope are called *Envelope-matters* (*Hüllen-stoffe*). The nucleus of acetic acid, $C^4H^4O^4$, is C^4H^4, and the envelope O^4; the nucleus-matters are C and H, and the envelope-matter is O; if, however, acetic acid be regarded as C^4H^3O,H^3O^3, the nucleus-matters are C, H, and O, and the envelope-matters are H and O.

Thirdly, we have to consider compounds of the nuclei and envelope-nuclei with other substances, organic or inorganic, products which may be called *Conjugated* or *Copulated Compounds* according to Gerhardt, or *Syndesmides* according to Laurent.

Thus, every primary nucleus forms a corresponding series of *Types*, which series may be designated as the *Primary Series*. The first type of this series is formed by the primary nucleus itself; the second, perhaps by: Nucleus + H; the third: Nucleus + H^2; the fourth: Nucleus + HO, the fifth: Nucleus + H^3O^2; the sixth: Nucleus + O^2; the seventh: Nucleus + O^4, &c.

After each primary nucleus, together with the series of its compounds, follow its *Secondary* or *Derived Nuclei*, which belong to the same type with itself. A primary nucleus may yield a number of secondary nuclei of the most various composition, according to the elements or compounds which wholly or partially replace the H of the primary nucleus.

Each of these secondary nuclei generally forms several compounds with envelope-substances, and hence are produced a number of *Secondary Series* equal to that of the secondary nuclei.

Thus the primary series of ethylene [= Vine], C^4H^4, has, among others, the following members: C^4H^4,O^2; C^4H^4,O^4; and the secondary series belonging to the secondary nucleus, C^4HCl^3, has the following corresponding members: C^4HCl^3,O^2; C^4HCl^3,O^4. — $C^4H^4O^2$ and C^4HCl^3,O^2 belong to the same type; so likewise do C^4H^4,O^4 and C^4HCl^3,O^4; and in this manner a type of the primary series may be repeated in the secondary series.

Lastly, the secondary nuclei frequently produce copulated compounds.

A primary nucleus together with its secondary nuclei, and all compounds yielded by the nuclei, both primary and secondary, or, in other words, the primary series, together with all the secondary series derived from the same nucleus, form a *Group*.

It appears then that all organic compounds may be first divided into different groups; each group resolves itself into the series of the primary nucleus and the series of the secondary nuclei; each series consists of members of different type; but the individual types are often repeated in the secondary series.

A further comparison of the members of different groups, one with the other, exhibits *Types in the wider sense of the word*. Thus the Nucleus-type includes all the nuclei, primary and secondary, of the various groups; the Alcohol-type, all these nuclei with addition of H^2O^2; *e. g.*, $C^{10}H^{10},H^2O^2$; $C^{32}H^{32},H^2O^2$, &c.; the monobasic acid type, the nuclei with addition of O^4; *e. g.*, C^2H^2,O^4; C^4H^4,O^4, &c. &c.—These types in the more general sense accord pretty nearly with Gerhardt's *homologous substances*, in which, however, certain restrictions are made in the proportion of C to H. (Gerhardt's *Chim. org.* 1, 25.)

VI. Suggestions for a New Chemical Nomenclature, particularly for Organic Compounds.

The daily increase in the number and complexity of chemical compounds forces upon us the conviction that arbitrary names based upon their origin, properties, historical circumstances, &c., are insufficient, and that the most characteristic appellations, those, namely, which denote stoïchiometrical composition, cannot be formed with our existing nomenclature, without producing words of intolerable length. A perfectly satisfactory name must denote, not only the nature of the components of a compound, but likewise the number of its atoms, and their mode of combination; it must be, as it were, a rational formula comprised in a word. By this means, even polymeric and metameric compounds will be distinguished one from the other, and only for isomeric compounds will a mode of distinction still remain to be sought.

To render such an attempt successful, without producing names of too great length, each element must be expressed by a monosyllabic word, and the number of atoms distinguished (as already effected by Laurent in a somewhat different way) by alteration of the vowels.*

Let	a	e	i	o	u	ai	aü	au	ö	ü
denote	1	2	3	4	5	6	7	8	9	0

The elements *in the free state* may be distinguished by the following names.

O = Ane;—H = Ale;—C = Ase;—B = Are;—P = Ape;—S = Afe;—J = Asche (long);—Br = Ame;—Cl = Ake;—F = Alfe;—N = Ate.

K = Pate (from *Pot*ash);—Na = Nate (from *Nat*ron);—L = Late (from *Lith*on);—Ba = Bare (from *Baryta*);—St = Stare (from *Stront*ian);—Ca = Care (from *Calc*ium);—Mg = Talke (from *Talk*);—La = Lante (from *Lanth*anum);—Ce = Zarme (from *Cer*ium);—Y = Garte (from *G*adolin and *Yttr*ium);—G = Gluke (from *Glyc*ium);—Al = Talme (from *Th*on and *Alum*en);—Zr = Zarke (from *Zirc*onium);—Th = Tarne (from *Th*orium);—Si = Kalse (from *Kies*el).

Ti = Manke (from *Menak*an);—Ta = Talte (from *Tantal*);—Wo = Wolfe (from *Wolfr*am);—Mo = Molde (from *Molybd*enum);—Va = Wante (from *Vanad*ium);—Cr = Krame (from *Chrom*ium);—U = Ranse (from *Uran*ium);—Mn = Ganne (from *Mangan*ese).

Ar = Karse (from *Arsen*ic);—Sb = Mante (from *Antimon*y);—Te = Tarle (from *Tellur*ium);—Bi = Marxe (from *Markas*it);—Zn = Zakke (from *Zinc*);—Cd = Galme (from *Galm*ei);—Sn = Stanne (from *Stann*um);—Pb = Plambe (from *Plumb*um);—Fe = Marte (from *Mars*);—Co = Smalte (from *Smalt*);—Ni = Nalke (from *Nickel*);—Cu = Carpe (from *Cupr*um).

Hg = Kwakke (from *Quick*silver);—Ag = Targe (from *Argent*um);—An = Galte (from *Gold*);—Pt = Plate (from *Plat*inum);—Pd = Palte (from

* The author's system of nomenclature is specially adapted to the German language, and could not be made available in English without many alterations, especially in the vowel-sounds used to denote numbers. It is sufficient, however, to give the original form, as there is but little probability that this or any similar system of nomenclature—which would in fact involve the acquisition of a new language—will ever be generally adopted. Nevertheless the system is well worthy of attention, if only for the ingenuity displayed in its construction. (For observations on the necessity of preserving a marked distinction between names and formulæ, *vid.* Dumas, *Leçons de Philosophie chimique.*) [W.]

*Palla*dium);—R=Prade (from *Rho*dium);—Ir=Parte (from *Irid*ium);—Os=Pasme (from Os*m*ium).

In combining the names of the elements, the final *ĕ* is dropped, and if the compound contains more than one atom of any element, the *a* in the name of that element is changed into the vowel which denotes the number of atoms present.

Thus: HO=Alan; HO^2=Alen; CO^2=Asen; SO^3=Afen; SO^3=Afin; S^2O^3=Efen; S^2O^5=Efun; S^2O^5=Ifun; S^4O^5=Ofun; ClO^7=Akaün; S^2Cl=Efak; SCl=Afak; PCl^3=Apik; PCl^5=Apuk; BF^3=Arilf; NH^3=Atel; NH^3=Atil; NH^4=Atol; NH^3,HCl or NH^4Cl=Atil-Alak or Atolak; KO=Patan; Al^2O^3=Telmin; Fe^2O^3=Mertin; Fe^3O^4=Mirton; Fe^2Cl^3=Mertik.

Since ü has the signification of *nothing*, all oxygen-compounds may be designated as *Ünide;* hydrogen compounds as *Ülide;* chlorine compounds as *Ükide;* sulphur-compounds as *Üfide;* iron-compounds as *Mürtide*, &c.—In a similar manner, the oxides of iron may be called *Mürtüníde*, its sulphur-compounds as *Mürtüfide*, &c.

Simple salts may be denoted as follows: KO,CO^2=*Patan-Asen;* BaO,SO^3=*Baran-Afin;* AgO,NO^5=*Targan-Atun;* $KCl,PtCl^2$=*Patak-Platek.*

If the proximate constituents of salts do not enter in equal numbers of atoms, the number of atoms must be expressed by a vowel, preceded or followed by a *j* (which letter does not occur in the name of any of the elements); *e.g.*, $KO,2CO^2$=*Patan-Ejasen;* $KO,3IO^5$=*Patan-Ijaschun;* $6PbO,NO^5$=*Jaiplamban-Atun.* The *j* precedes or follows the multiplying vowel, according as the name of the element begins with a consonant or a vowel.

Examples of double salts: KO,SO^3+MgO,SO^3 or $KO,MgO,2SO^3$=*Patan-Afin-Talkan-Afin*, or better: *Patan-Talkan-ejafin.*

In compounds containing water, the intimately combined water which in formulæ is expressed by HO, must likewise be distinguished by the name, from the less intimately combined water of crystallization which is expressed symbolically by Aq.—HO=*Alan*, 2HO=*Elen*, &c.; but Aq.=*Was* (from *Wasser*, the *a* to be sounded *long*). The number of atoms may be expressed as follows:

Was	Wes	Wis	Wos	Wus	Wais	Waüs	Waus	Wös	Wasü
1	2	3	4	5	6	7	8	9	10
Wasa	Wase	Wasi	Waso	Wasu	Wasai	Wasaü	Wasau	Wasö	Wesü
11	12	13	14	15	16	17	18	19	20
Wesa	Wese	Wesi	Weso	Wesu	Wesai	Wesaü	Wesau	Wesö	Wisü
21	22	23	24	25	26	27	28	29	30

Accordingly: $NaO,SO^3+10Aq.$=*Natun-Afin-Wasü;*—$CuO,NO^5+6Aq.$=*Carpan-Atan-Wais;*—$2NaO,HO,PO^5+24Aq.$=*Jenatan-Alan-Apun-Weso;*—$3NaS,SbS^5+18Aq.$=*Jinataf-Mantuf-Wasau;*—and, to take one of the most complicated compounds: $NH^4O,Al^2O^3,4SO^3+24Aq.$=*Atolan-Telmin-Ojafin-Weso.* This last expression is certainly longer than *ammonia-alum;* but it is shorter than *crystallized ammonia-alum*, and even than the formula;—for the whole word contains ten syllables; whereas the formula, when read, contains eighteen syllables, and the composition is expressed quite as precisely by the word.

I do not see many sources of inaccuracy in this attempt. An objection may, it is true, be raised to the expression of the numbers of atoms

by ten vowels and diphthongs, which in pronunciation are not always very clearly distinguished. But the chemist, who knows how much the designation of a compound depends upon the exact pronunciation of these sounds, will take care to sound them correctly. If we were to stop the number of distinct sounds at u=5, we should be obliged, in expressing higher numbers, to make use of the inconvenient quintal system, in which, for example, we should have, *anu*=50, *and*=60, *ane*=70, &c., and in which 18Aq. would be expressed by *wisi*, and 24Aq. by *woso*. This system would be difficult of application. Moreover, the use of diphthongs introduces more variety into the names.

A confusion of the consonants, and consequently of the elements, is not so much to be apprehended.

Finally, the hitherto unaccustomed sound of these words would by practice become as familiar to us as the chemical formula in which the elements are denoted by letters, the only difference being that actual figures are more easily understood than numbers expressed by vowels.

In working out the details of this nomenclature, it would doubtless be found that many additions and improvements were necessary. At present, however, I content myself, so far at least as the inorganic part is concerned, with introducing this attempt, in its principal features as above presented, to the notice of the chemical world, and shall, perhaps, at a future opportunity develop it in detail, availing myself of all additions and corrections that may be suggested. I should not indeed have brought it forward on the present occasion, but for two reasons: first, that I have the satisfaction of observing that the atomic weights adopted in this Hand-book meet with continually increasing acceptation, whereby the obstacles in the way of a generally received stoïchiometrical nomenclature are gradually being removed,—and secondly, that there appears to be an absolute necessity for the immediate adoption of such a nomenclature in the case of organic compounds, in order that we may at least be able to give names founded on stoïchiometrical relations, to compounds which are yet undiscovered or but little known.

In the nomenclature of organic compounds, something more is required than the names of the elements and the expression of the numbers of their atoms by vowels—the numbers being, in fact, too large for this mode of expression. If, for example, we would designate *Paraffin* in this manner, we should obtain the expression: *Osan-Ulii*, which, though a short word, would not be easily reduced to numbers. The same inconvenience is experienced with compounds, both organic and inorganic, which contain more than 9 At. of water of crystallization; these, however, seldom come into comparison with organic compounds containing more than 9 At. of carbon and hydrogen.

For these reasons, it is further necessary to give a distinct name to each primary nucleus, so that its name may at once express the large number of carbon- and hydrogen-atoms which it contains. The number of those atoms which either alter the primary nucleus by substitution, or attach themselves to it as an envelope, seldom exceeds eight, and is therefore easily expressed by vowels. Secondary nuclei, such as the various kinds of sugar, which contain a large number of atoms capable of replacement, are perhaps best expressed by particular names. In order that the nuclei may be readily distinguished in the compounds which they form, their names must begin with a consonant and end with a consonant followed by a short *e;* for the hitherto received terminations in *en* or *um* might be mistaken for 2O or 5Br. In order, therefore, that the nuclei may be readily distinguished from metals, their names are best formed,

not with the vowels *a* and *e*, but with other vowels or diphthongs; for as the metals rarely enter into combination in more than 2 At., their names almost always contain the vowel *a* or *e*,—and as organic nuclei rarely, if ever, enter as more than 1 At., they retain the vowel or diphthong originally assigned to them. Lastly, if we even regard Stilbene (*Stilbe*), $C^{28}H^{12}$, as a compound of 2 At. Benzene (*Bunze*), $C^{14}H^{6}$, it may still be allowed to retain a particular name, the more especially as it is not yet satisfactorily proved to be a double atom of benzene.

In carrying out these principles, it is, unfortunately, necessary to alter more or less the names hitherto given to the nuclei, and, in so doing, we can pay but slight regard to etymology. The following are examples of the alterations required: Palene or Methylene, $C^{2}H^{2}$, into *Forme;* Ethene or Ethylene, $C^{4}H^{4}$, into *Vine;* Butyrene, $C^{8}H^{8}$, into *Bute;* Amylene or Mylene, $C^{10}H^{10}$, into *Myle;* Phenene, $C^{12}H^{6}$, into *Fune;* Benzene, $C^{14}H^{6}$, into *Bunze;* Salene, $C^{14}H^{8}$, into *Tole* (from Toluol); Cinnamine or Styrol, $C^{16}H^{8}$, into *Styre*, &c.

When a primary nucleus is transformed into a secondary nucleus, the final *e* is dropped, and the elements which replace the hydrogen are annexed, the number of their atoms being denoted by the appropriate vowel. Thus the secondary nucleus, $C^{4}H^{3}O$, of *Vine*, which is supposed to exist in acetic acid, is called *Vinan;* the secondary nuclei of *Vine*, produced by chlorine, viz., $C^{4}H^{3}Cl$; $C^{4}H^{2}Cl^{2}$; $C^{4}HCl^{3}$, and $C^{4}Cl^{4}$, are denoted respectively by: *Vinak*, *Vinek*, *Vinik*, and *Vinok*. Indigo, $C^{16}H^{5}NO^{2}$, regarded as a secondary nucleus, derived from *Styre*, $C^{16}H^{8}$, is called *Styraten*. In these names, the accent is to be laid on the syllable denoting the nucleus.

Since the hydrogen in the nucleus is likewise often replaced by NO^{4} and NH^{2}, perhaps also by NH and by SO^{2}, it is advantageous to express these compounds by the monosyllables, *art* (from Nitro), *amt* (from Amidogen), *ant*, and *aft*. Thus, for example, Nitrobenzide, $C^{12}H^{5}NO^{4}=C^{12}H^{5}X=$*Funart;* Binitrobenzide, $C^{12}H^{4}X^{2}=$*Funert;* Phthalimide, $C^{16}H^{5}AdO^{2}=$*Styramton*; Sulphobenzide, $C^{12}H^{6}(SO^{2})=$*Funaft*.

If the nuclei are surrounded with envelopes, the enveloping substances are placed before the nucleus, the vowel following the consonant; e. g., *na* instead of *an; la* instead of *al*, &c. Thus marsh-gas, $C^{2}H^{3},H^{2}=$ *Leforme;* aniline, $C^{12}H^{5}N,H^{2}=$*Lefunat;*—aldehyde, $C^{4}H^{4},O^{2}$, or $C^{4}H^{3}O,HO$ $=$*Nevine* or *Lanavinan;* phenous acid, $C^{12}H^{6},O^{2}$ or $C^{12}H^{5}O,HO=$*Nefune* or *Lanafunan;*—chlorophenessic acid, $C^{12}H^{4}Cl^{2},O^{2}=$*Nefunek;* bromophenissic acid, $C^{12}H^{3}Br^{3},O^{2}=$*Nefunim;*—chlorophenussic acid, $C^{12}HCl^{5},O^{2}$ *Nefunuk;*—nitrophenissic acid or picric acid, $C^{12}H^{2}X^{3},O^{2}=$*Nefunirt;*—chloracetamide, $C^{4}Cl^{3}Ad,O^{2}=$*Nevinamtik;* — acetic acid, $C^{4}H^{4},O^{4}$ or $C^{4}H^{3}O,HO^{3}=$*Novine* or *Lanivinan;* acetate of potash, $C^{4}H^{3}K,O^{4}$ or $C^{4}H^{3}O,KO^{3}=$*Novinepat* or *Patinvinan*. The oil of olefiant gas, $C^{4}H^{4},Cl^{2}$ or $C^{4}H^{3}Cl,HCl=$ *Kevine* or *Lakavinak;* sesquichloride of carbon, $C^{4}Cl^{4},Cl^{2}=$ *Kevinok;* alcohol, $C^{4}H^{4},H^{2}O^{2}$ or $C^{4}H^{3}O,H^{3}O=$ *Lenevine* or *Linavinan;*—so likewise mercaptan, $C^{4}H^{4},H^{2}S^{2}$, or $C^{4}H^{3}S,H^{3}S=$*Lefevine* or *Lifavinof*, &c.

With the exception of the new names of the nuclei, which may perhaps be thought preferable to the old ones, it is not my intention formally to introduce even the organic part of the above described nomenclature, but merely to insert the new names in their respective places, within three-cornered brackets, in order that some idea may be formed of their probable adaptability.

This nomenclature by no means excludes particular names for types, both of the envelope-nuclei and of copulated compounds (*e. g.*, Aldides,

Alcohols, Ketones, Compound Ethers); on the contrary, the designation of the more complicated compounds, such as the oxygen-acid ethers of copulated acids, &c., are facilitated by its use. [For further details, see these compounds.]

VII. General View of Types.

A. Nuclei.

a. Primary Nuclei.

These nuclei consist wholly of carbon and hydrogen. In those which are known in the separate state, the number of carbon-atoms varies from 2 to 48, and the number of hydrogen-atoms is to that of carbon-atoms, at least as 1 to 3, and at most as 1 : 1.—Thus, Chrysene = $C^{24}H^{8}$; Anthracene, $C^{30}H^{12}$; Stilbene, $C^{28}H^{12}$; Naphthene, $C^{20}H^{8}$; Phenene, $C^{12}H^{6}$; Terebene, $C^{20}H^{16}$, &c. Further, Palene or Methylene = $C^{2}H^{2}$; Ethene or Ethylene, $C^{4}H^{4}$; Butyrene, $C^{8}H^{8}$; Amylene, $C^{10}H^{10}$; Oleene, $C^{12}H^{12}$; Cetene, C^{32},H^{32}, &c. Many primary nuclei are not yet known in the separate state; *e.g.*, Benzene, $C^{14}H^{6}$, which must be supposed to exist in benzoic acid, &c.—In certain primary nuclei, not yet known to exist in the separate state, *e. g.*, in that from which sugar is derived, the number of H-atoms exceeds the number of C-atoms.

Most of the known *Hydrocarbons* are primary nuclei; some, however, are compounds of primary nuclei with two additional atoms of hydrogen; *e. g.*, Marsh-gas, $C^{2}H^{4}$, which may be regarded as a compound of methylene with H^{2}. As these two kinds of hydrocarbons cannot be distinguished with certainty, it will be most convenient to consider them together.

These hydrocarbons consist, either of gases distinguished by great illuminating power, or of thin oily volatile liquids called *Volatile Oils;* or of crystalline, fusible, and volatile bodies called *Camphors* or *Stearoptenes;* or of waxy and resinous bodies, like Paraffin, Ozokerite, and Caoutchouc.

The following table contains the best known hydrocarbons, arranged in the ascending order of the carbon- and hydrogen-atoms.

The determination of these numbers is effected by the following methods :

1. By ascertaining from what other compounds a certain hydrocarbon is produced. Thus, when alcohol is distilled with oil of vitriol, and likewise when fusel-oil is distilled with phosphoric acid, a hydrocarbon is produced containing carbon and hydrogen in equal numbers of atoms. But since alcohol is $C^{4}H^{6}O^{2}$, and fusel-oil is $C^{10}H^{12}O^{2}$, we conclude that the hydrocarbon derived from alcohol (olefiant gas) = $C^{4}H^{4}$, and that which is produced from fusel-oil (amylene or mylene) = $C^{10}H^{10}$.

2. By determining in what proportion a hydrocarbon combines with other substances. and in what proportion the hydrogen-atoms are substituted therein. Since, for example, oil of turpentine, regarded as $C^{20}H^{16}$, takes up only 1HCl, its formula cannot very well be $C^{10}H^{8}$, or $C^{5}H^{4}$, as, in that case, 1 At. oil of turpentine would take up only a fraction of an atom of hydrochloric acid, viz., one-half or one-fourth. (In some cases of this kind, however, it is thought preferable to suppose that 2 or 4 At.

of a hydrocarbon take up 1 At. of another substance.)—Again, as in phenene, $C^{12}H^6$, 1H is replaced by 1X, the formula of phenene cannot very well be reduced to C^6H^3, or C^4H^2, or C^2H.

3. By comparing the observed vapour-density of a hydrocarbon with that which is given by calculation from the assumed formula, on the supposition that a diatomic gas should be produced. Thus, according to the numbers adopted in the present work, $C^{12}H^6$ should give the following vapour-density: 12 vol. C-vapour=4·9920; 6 vol. H-gas=0·4158; sum = 5·4078; and 5·4078 + 2 + 2·7039 = calculated vapour-density; the observed density is 2·77. The formula C^6H^3 would make the density only half, and the formula C^2H only one sixth as great.

4. By comparing the observed boiling point of a hydrocarbon with that which it should have, according to calculation. In the column headed "calc.' in the following table, the starting point is the boiling point of oil of turpentine ($C^{20}H^{16}$), the mean value of which is 160°. From this the several numbers are calculated according to Gerhardt's law (p. 57), that each addition of 2C to a compound raises the boiling point to 35°, and each substraction of 2C lowers it 35°; while, on the other hand, each addition of 2H lowers the boiling point 15°, and each subtraction of 2H raises it 15°. For the present, we must content ourselves with a moderately near approximation, as, indeed, the table shows.—If we find, for example, that in distilling fusel-oil with phosphoric acid, we first obtain an oil boiling at 35°, and regarded as Amylene, $C^{10}H^{10}$, but afterwards an oil which boils at 160°, we must suppose that 2 At. Amylene have united and formed 1 At. Paramylene, $C^{20}H^{20}$.

C	H	Boiling point. calc.	Obs.	at 0°	
2	2	−50°	?	gas	Methylene = Palene (= *Forme*); not satisfactorily known in the free state.
2	4	−65°	?	gas	Marsh gas = C^2H^2,H^2.
4	4	−30°	?	gas	Olefiant gas = Ethene or Ethylene (= *Vine*).
8	8	+10°	−10°?	gas	Faraday's most volatile empyreumatic oil, probably = Butyrene or Butylene (= *Bute*).
10	10	30°	+39°	oil	Amylene = Mylene (= *Myle*, probably = Caoutchene.
12	6	95°	86°	camphor	Benzine = Phenene or Phenylene (= *Fune*) = Faraday's oil-gas camphor.
12	8	80°	135°	oil	Mesitylene (probably = $C^{18}H^{12}$).
12	12	50°	55°	oil	Oleene (= *Prone*).
14	8	115°	114°	oil	Benzoene = Toluol = Dracyl (= *Tole*); also Retinnaphtha which boils at 106°.
14	12	85°	85°	oil	Most volatile portion of Rock-oil.
16	8	150°	146°	oil	Cinnamene = Styrol (= *Styre*).
16	16	90°	115°	oil	Naphthene, in rock-oil, probably = Elaene (= *Pryle*), which boils at 150°.
18	12	155°	153°	oil	Cumene (= *Kume*), probably = Retinyl, which boils at 150°.
18	16	125°	135°	oil	Campholene (= *Fole*).
20	8	220°	221°	camphor	Naphthalin = Naphthene (= *Nafte.*)
20	10	205°	200°	camphor	Scheererite.
20	14	175°	175°	oil	Cymene = Camphogene (= *Cyme*) probably also = Tolene, which boils at 170°.
20	16	160°	142°	oil	Neutral oil of cloves.
20	16	160°	156°	oil	Oil of turpentine in its different isomeric conditions: Savine oil, Juniper oil, Borneene, Empyreumatic oil of Birch.
20	16	160°	165° to 180°	oil	Oils of Lemons, Pepper, Elemi, and Parsley. Carvene.

C	H	Boiling point. calc.	Obs.	at 0°	
20	18	145°	163°	oil	Menthene.
20	20	130°	160°	oil	Paramylene.
24	8	290°	?	camphor	Chrysene.
24	22	200°	190°	oil	Naphthol in rock-oil.
28	12	330°	?	camphor	Stilbene.
30	10	380°	above 300°	camphor	Idrialin, probably = Succisterin.
20	12	365°	above 300°	camphor	Anthracene, with which also Pyrene is isomeric.
30	24	275°	260°	oil	Oil of Copaiba and Oil of Cubebs, probably = Cedrene, which boils at 237°.
32	16	370°	238°	oil	Retinol.
32	32	250°	275°	oil	Cetene. The formula $C^{32}H^{32}$ probably belongs also to the following substances: Wine-oil camphor, 260°; Wine-oil, 280; Rose-camphor, 280°.
36	22	395°	360°	camphor	Phylloretin (?)
36	32	320°	360°	camphor	Tekoretin (?)
38	38	310°	315°	oil	Heveene (?)
40	32	390°	315°	oil	Colophene; Petrolene, which boils at 280°, likewise belongs to this place, so far as its other properties are concerned.
40	40	330°	300°	solid	Ozokerite (?)
48	50	395°	380°	camphor	Paraffin, probably $C^{48}H^{46},H^{2}$.

Oil of wax, Aurad, Hatchettin, Caoutchouc, &c., contain xCH; Fichtelite, $xC^{4}H^{3}$; Hartite, $xC^{5}H^{4}$; but with respect to these and a few other hydrocarbons, we are in want of observations of the facts 1—4, in order to determine, with any degree of certainty, the number of atoms which they contain.

From the table just given, the following conclusions may be drawn: Carbon generally combines with hydrogen in very simple numerical proportions, and most frequently in the ratio of 1 : 1; and thus there is produced a series of polymeric compounds, all of which contain 6 pts. C to 1 pt. H, while the individual atoms in some cases contain 2, in others 4, 8, 10, 12, 16, 20, 32, 38 or 40 At. C and H. To this series, also, belong Oil of Wax, Aurad, Hatchettin, and Caoutchouc, in which the number of atoms cannot at present be determined.—The ratio of 2 : 1 is also of frequent occurrence, as in $C^{12}H^{6}$ and $C^{16}H^{8}$;—also that of 3 : 1, as in $C^{24}H^{8}$ and $C^{30}H^{10}$;—that of 3 : 2 in $C^{18}H^{12}$;—that of 5 : 2 in $C^{20}H^{8}$ and $C^{30}H^{12}$;—that of 5 : 4 in $C^{20}H^{16}$; $C^{30}H^{24}$, and $C^{40}H^{32}$. More complex relations are of less frequent occurrence.

Those hydrocarbons which contain not more than 8 At. carbon, are gaseous at 0°, and may be reduced by cooling and pressure, to very thin oils. Those which contain more than 8 atoms of carbon, are either oily or solid, and in the latter case, crystalline and camphor-like.

These compounds are more inclined to the oily and less to the camphoroidal state, in proportion as the number of elementary atoms which enter into the composition of the compound atom is smaller, and as the carbon predominates less over the hydrogen. Thus, all hydrocarbons which may be represented by the formula xCH are oily, excepting Wine-oil camphor, Rose-camphor, Aurad, Ozokerite, Hatchettin, and Caoutchouc, all of which, to judge from their boiling points, must contain a large number of elementary atoms; Paraffin also, $C^{48}H^{50}$, doubtless owes its camphoroidal condition to the same cause.—On the other hand, all

hydrocarbons in which the ratio of the C-atoms to the H-atoms = 2 : 1, or 5 : 2, or 3 : 1, are camphoroidal, even when the number of elementary atoms contained in their compound atoms is comparatively small; $C^{12}H^{6}$, for example, forms a camphor. The only exception is the oily substance, Retinol, $C^{32}H^{16}$.

Until lately, the non-gaseous and non-resinous hydrocarbons were included in the same family with a number of compounds of similar nature, but containing small quantities of oxygen, or sulphur, or of sulphur and nitrogen, besides carbon and hydrogen. This family is that of the *Volatile, Ethereal,* or *Essential Oils in the wider sense,* which, according as their melting point is below or above 0°, are divided into *Volatile Oils proper,* and *Camphors* or *Stearoptenes.*

As the composition of many compounds included in this family, which are frequently mixtures of true hydrocarbons with oxidized hydrocarbons, is not yet sufficiently known to admit of complete and exact separation, and, moreover, their formation and preparation, their properties, decompositions, and combinations present many points of resemblance, it will be best to introduce in this place a general view of volatile oils in the wider sense.

Volatile Oils in general.

Preparation: Fr. Hofmann. *Opuscula phys. chim.* Lib. 1, n. 1, p. 1.—Demachy. *Laborant im Grossen,* 1, 235.—Dehne. *Crell, chem. J.* 3, 6.—Soubeiran. *J. Pharm.* 23, 537; also *Ann. Pharm.* 25, 241; also *J. pr. Chem.* 13, 123.—Raybaud. *J. Pharm.* 20, 437.—Bley. *Repert.* 48, 92.—Dann & Völter. *Repert.* 55, 354.—Van Hees. *Pharm. Centr.* 1847, 380.—Schaarling. *J. pr. Chem.* 50, 375.—Cahours. —On the light oils obtained in the Distillation of Wood. *Compt. rend.* 30, 126.—Stenhouse.—On the oils produced by the action of Sulphuric acid on different vegetables. *Ann. Pharm.* 74, 278; *Chem. Gaz.* 1850, 319.

Specific Gravity: Martius. *Repert.* 39, 234.—Brandes & Reich. *Brand. Arch.* 21, 155.—Guibourt & Chardin Hadancourt. *J. chim. méd.* 7, 596.—Van Hees. *Pharm. Centr.* 1847, 380; *Jahresber.* 1847-8, 708; *Arch. Pharm.* [2], 61, 18; *Pharm. Centr.* 1850, 157; *Jahresber.* 1850, 486.

Chemical Relations, Composition: Boerhaave. *Elementa Chemiæ,* 2, 124.—Gren. *Handb. der Chem.* 2, 217.—Fourcroy. *Scher. J.* 3, 539.—Robiquet. *Ann. Chim. Phys.* 15, 27; also *N. Tr.* 5, 2, 103.—Saussure. *Ann. Chim. Phys.* 13, 259, and 337; also *Schw.* 28, 389; 29, 165 and 30, 364; also *N. Tr.* 5, 1, 221 and 5, 2, 112.—Göbel. *N. Tr.* 5, 2, 16.—Dumas. *Ann. Chim. Phys.* 48, 430; also *Schw.* 66, 87. *Ann. Chim. Phys.* 50, 182 and 225; also *Schw.* 66, 73 and 89; also *Ann. Pharm.* 5, 5 and 6, 257; also *N. Tr.* 26, 1, 231. *J. Pharm.* 21, 191; also *Ann. Pharm.* 5, 5 and 6, 257; also *N. Tr.* 26, 1, 231. *J. Pharm.* 21, 191; also *Ann. Pharm.* 15, 158; also *J. pr. Chem.* 4, 437.—Dumas & Peligot. *Ann. Chim. Phys.* 57, 334; also *J. pr. Chem.* 4, 386.—Sell & Blanchet. *Ann. Pharm.* 6, 259.—Blanchet. *Ann. Pharm.* 7, 154.—Kane. *Phil. Mag. J.* 13, 437.—Zeller. *Jahrb. f. Pharm.* 18, 1, 73, 153, 217, 281, 353; 19, 1, 65.

Alterations produced by Cold, Light, and Air: Margueron. *J. Phys.* 45, 136.—Tingry. *J. Phys.* 56, 161.—Seb. Bucholz. *Taschenb.* 1785,

101.—Bizio. *Brugn. Giorn.* 19, 360.—Unverdorben. *Pogg.* 8, 483.—Th. Saussure. *Ann. Chim. Phys.* 49, 225; also *Pogg.* 21, 370; also *Ann. Pharm.* 3, 157.

Decomposition by Distillation with Earthy Substances: Hasse. *Crell, Ann.* 1786, 2, 36 and 128.—W. B. Trommsdorff. *Diss. de oleis essentialibus, &c.* Erf. 1766.

Decomposition by Nitric Acid: Olaus Barrichius. *Thom. Bartholini Acta med. et philos.* Hafn. 1671.—Fr. Hofmann. *Opusc. phys. chim.* Lib. 1, Obs. 3.—Geoffroy. *Mém. de l'Acad. de Paris,* 1726, 95.—Rouelle. *Ibid.* 1747, 43.—Scheele, *Opusc.* 2, 206.—Hasse. *Crell N. Endtdeck.* 9, 42; and *Crell Ann.* 1785, 1, 422.—Kels. *Crell Ann.* 1785, 1, 302.—Gren. *Crell Ann.* 1786, 2, 151.—Dollfuss. *Crell Ann.* 1787, 1, 443.—Proust. *N. Gehl.* 6, 376.—Grotthuss. *N. Gehl.* 8, 709.—Bonastre. *J. Pharm.* 11, 529; also *N. Tr.* 12, 1, 180.

Action of Sulphuric and Hydrochloric acid: Hasse. *Crell Ann.* 1786, 2, 36 and 128.—Achard. *Chem. phys. Schriften,* 305.

Action of Iodine: Tuchen. *Kurze übersicht der wichtigsten Reagentien,* s. 56.—Walcker. *Pogg.* 6, 126.—Flashoff, Zeller. *Br. Arch.* 33, 225 and 36, 257.—Winckler. *Repert.* 32, 271 and 33, 185.—Guyot. *J. scienc. phys.* 5, 230.—Well. *Ann. Pharm.* 65, 230; also *Pharm. Centr.* 1848, 230; also *Jahresb.* 1847-8, 709.

Volatile, Ethereal, Essential, or *Distilled Oils in general* are organic compounds, either consisting wholly of carbon and hydrogen, or of the same elements with addition of small quantities of oxygen, sulphur, or nitrogen; mostly colourless; of specific gravity from 0·627 to 1·094; rarely heavier than water, and then only in a slight degree; capable of assuming the crystalline form at various temperatures from below −27° to + 240°; of thin oily consistency at higher temperatures; and wholly or partly volatile at still higher temperatures; they leave a transient oily stain on paper; have a peculiar and generally pungent odour, agreeable in some cases, repulsive in others; and a strong, mostly warm and aromatic taste;—they burn with a bright but very smoky flame, and dissolve very sparingly in water, but readily in alcohol and ether.

If the volatile oil is liquid at 0°, it is called *Volatile Oil proper, Elaioptene* (Berzelius) or *Hygrusin* (Bizio); if it does not melt till heated above 0°, it is distinguished by the term *Camphor* (Naumann, *Chymia Medica,* 1751, 1, 238), *Camphoride* (Trommsdorff), *Stearoptene* (Berzelius), or *Stereusin* (Bizio).

History. Boerhaave regarded volatile oils as compounds of a resinous substratum with a peculiar odorous principle, *Spiritus Rector Aroma,* which he supposed to be highly volatile and scarcely ponderable, and to be the cause of most of the odours of organic bodies. At present, however, it is supposed, as first suggested by Gren and Fourcroy, that the peculiar odour of volatile oils is a property belonging to the bodies themselves.

Sources. 1. In the animal kingdom, in ants, in castoreum, in ambergris, in the stinking liquid of the *Viverra Putorius,* and probably in many other odorous animal products.—2. In the vegetable kingdom, in very large quantity, in almost all parts of the plant, as in the wood and bark of the stem and root; under the epidermis of the leaves, calices, petals, fruits, &c.; in the different coatings of the seed, and in the cellular

tissue of the seed-vessels; rarely in the albumen, and sometimes even in the embryo of the seed. (Wahlenberg, *N. Gehl.* 8, 134.)—3. In the mineral kingdom, in rock-oil.

Many volatile oils are *artificially formed* by the decomposition of other compounds, mostly organic. To this class belong the volatile oils produced by heat, by fermentation, by sulphuric or phosphoric acid, and those obtained from cast-iron.

1. In the *Dry* or *Destructive Distillation* of most other organic compounds, there passes over a watery liquid, together with a brown oily liquid, sometimes of thin, sometimes of thick consistence, which is a mixture of various volatile oils, resins, and other substances. The oils thus produced are called *Empyreumatic Oils.* (*Brenzliche, brandige, oder empyreumatische Oele, Pyrelaine*, pp. 79, 80, 81.) By repeated distillation with or without water, the empyreumatic oils may be freed from resins, and obtained in the form of thin, colourless fluids. By distillation over lime or potash, oils which do not combine with those alkalis may be freed from acetic and various empyreumatic acids; similarly, by distillation over dilute sulphuric acid, they may be freed from ammonia and certain volatile alkaloids, which are likewise formed in the dry distillation. The product thus obtained is either a simple empyreumatic oil, or a mixture of several; the mode of separating them in the latter case will be explained when we come to speak of the individual oils.

These empyreumatic oils also are either pure hydrocarbons, such as Eupione, or oxidized hydrocarbons, like Creosote; in like manner, some of them are oils properly so called, such as those just mentioned, while others are camphors or stearoptenes, like Naphthalin.

Many empyreumatic oils are produced by distilling organic compounds with excess of baryta, lime, anhydrous phosphoric acid, or chloride of zinc. The two former bodies serve to withdraw the whole or the greater part of the oxygen from the organic compound in the form of carbonic acid, the two latter to remove it in the form of water.

2. *Volatile oils produced by Fermentation.*—Many volatile oils appear to be formed in the vinous fermentation, and other similar processes of decomposition of inodorous parts of plants,—*e. g.*, fusel-oil (which, however, is an alcohol), and the oils obtained by leaving *Hb. Centaur. min.*, *Farfaræ, Marubii, Trifol, fibrini*, &c., to ferment in contact with water, and distilling the fermented mass.

3. *Volatile oils produced by Sulphuric acid.*—To this class belong Oil of Wine, produced by the distillation of alcohol with excess of oil of vitriol, Furfurol, and other oils of similar nature, which pass over when dilute sulphuric acid (with or without addition of oxide of manganese) is distilled with sawdust, gluten, starch, sugar, &c.

4. *Volatile oils produced by Phosphoric acid.*—Peppermint-camphor distilled with phosphoric acid is converted, with loss of water, into Menthene, and Ethal into Cetene.

5. When cast-iron is dissolved in dilute hydrochloric or sulphuric acid, hydrogen gas passes over impregnated with the vapour of a volatile oil.

6. The volatile oils of *Spiræa ulmaria* and *Gaultheria procumbens* may likewise be obtained by artificial processes.

Those volatile oils which exist ready-formed in plants and animals (generally enclosed in cells) are obtained by one or other of the following methods.

1. *By Pressure.*—This method succeeds only with certain parts of plants which are very rich in oil, such as lemon and orange-peel.

2. *By Distillation*, generally with addition of water.—Heating without water is apt to produce charring and admixture of empyreumatic oils. The substances containing the volatile oil are either mixed with water in a large still or retort, and distilled after sufficient maceration; or they are placed in the dry state on an upper perforated base of the still, and subjected to the action of vapour of water. Although the boiling point of most volatile oils is above that of water, they nevertheless volatilize at 100°, in consequence of the adhesion of the oil-vapour to the vapour of water produced at that temperature. (I., 265 and 266) In the distillation of the less volatile oils, however, it is usual to add common salt to the water, in order to raise the temperature a few degrees, and thereby increase the tendency of the oil to pass over with the aqueous vapour. The vapours condense in the cooling tube or receiver, which is kept cold for the purpose; and the water takes up as much of the oil as it is capable of dissolving. If the quantity of oil present is more than sufficient to saturate the water, the excess separates out; in the contrary case, the distillate is *cohobated;* that is to say, the water containing the oil in solution is distilled with a fresh quantity of the substance which contains the oil, and thereby made to take up a double quantity of oil. A more abundant product is likewise obtained by distilling the original vegetable substance, not with pure water, but with water which has previously been used for the same distillation, and is therefore saturated with oil.—If the oil which passes over readily solidifies, the cooling tube must not be kept at a very low temperature.—The oil which collects either at the top or at the bottom of the water is separated mechanically from the water. This separation may be for the most part effected during the distillation by the use of the *Florentine Bottle* (*Florentiner Flasche*), and other apparatus contrived for the purpose by Chevallier (*J. chim. méd.* 2, 66), Brandes (*N. Br. Arch.* 14, 189), Desmarest (*J. Pharm.* 26, 697), and Häusler (*Jahrb. pr. Pharm.* 7, 96).

Many plants yield a larger quantity of oil after drying; and when distilled in the fresh state, with cold water, they yield a comparatively large quantity of oil together with turbid water; but if covered with boiling water and then distilled, they yield clear water and less oil. The cause of this difference is, that when the plant is dried, or immersed in cold water containing air, the oil oxidizes, and is thereby rendered less soluble in water; hence it forms a poorer and turbid solution, and for the most part separates out. (Desmarest, *J. Pharm.* 19, 163; *abstr. Ann. Pharm.* 9, 291.)

Volatile oils obtained by distillation, and likewise the water which passes over with them, have at first an unpleasant, empyreumatic odour, which, however, is not permanent.

3. Many strongly smelling parts of plants yield no volatile oil, even by repeated cohobation with water, probably because the quantity contained in them is too small, or because the oil is too soluble in water, or too much inclined to decompose by the action of air and heat; *e.g.*, the flowers of many kinds of *Narcissus* and *Hyacinth;* of *Polyanthes Jonquilla, Viola odorata, Jasmium off., Philadelphus coronarius, Tilia Europæa, Reseda odorata, Heliotropium Europæum.* Such flowers, placed in layers between cotton soaked in olive oil, impart their perfume to the oil.

From some of them it has been found possible to extract the odori-

ferous principle in the separate state. Robiquet (*J. Pharm.* 21, 334) exhausted the fresh corollas of *Polyanthes Jonquilla* with ether in compression-filters; separated the upper yellow ethereal stratum of liquid from the lower, watery layer; distilled the ether from the upper liquid at a gentle heat; and obtained a residue consisting of crystalline nodules, together with a mother-liquid, which, when evaporated in the air gave off a strong and agreeable odour of jonquils. The crystalline nodules, when purified, formed an inodorous camphor; and it appeared to Robiquet, that the odoriferous oil was converted into this camphor by exposure to the air.—L. A. Buchner (*N. Br. Arch.* 8, 70) obtained similar results by applying Robiquet's process to the flowers of *Philadelphus*, *Tilia*, and *Reseda*.

4. The less volatile oils, and more especially the camphors, are likewise frequently extracted by alcohol or ether, from which they are afterwards separated by evaporation and cooling.

Many gum-resins, such as myrrh, do not yield the oil which they contain, or at least yield it very imperfectly, by distillation with water, because it is enveloped in gummy matters. To extract the oil from these gum-resins, they are pulverized and then exhausted three times with an equal quantity of cold alcohol, agitating frequently, and leaving the whole to stand for some time; the filtered tincture is then poured into a tubulated retort, both apertures of which are left open, and left for some months at a temperature of 12°—21°, till the greater part of the alcohol is evaporated (if heat were applied, the oil would likewise pass over). The turpentine-like residue is then covered with water, and distilled after twelve hours, whereupon the oil passes over in abundance. (Bonastre, *J. Pharm.* 17, 108; also *N. Tr.* 24, 1, 270.)

The product obtained by either of these three modes of preparation rarely consists of a simple volatile oil, but generally of a mixture of two or more oils. The lighter and more volatile of these is usually a pure hydrocarbon; the other is either an oil containing oxygen, or a camphor. These bodies are sometimes distinguished by their melting points: thus, a volatile oil, properly so called, often holds a camphor in solution, and the latter crystallizes out on cooling, especially if part of the volatile oil (which is more easily vaporized) has been previously driven off. Sometimes again they are distinguished by their different volatility; when such a mixture is distilled, the boiling point is at first low, but rises as the quantity of the more volatile oil in the residue diminishes, till at length, when the whole of the latter has passed over (together with a considerable quantity of the more fixed oil), the boiling point no longer rises, but remains constant. In such cases, the more volatile oil generally consists wholly of carbon and hydrogen, while the more fixed oil likewise contains oxygen. The former may be distilled without decomposition over fused hydrate of potash; but the more fixed oil when thus treated, takes up an additional quantity of oxygen from the water of the hydrate of potash (liberating the hydrogen), and is converted into an acid which remains combined with the potash. Hence to separate the non-oxygenated oil from such a mixture, it is partly distilled so as to leave behind the greater part of the more fixed oil, and the portion which first passes over is made to drop slowly through the tubulus of another retort upon hydrate of potash kept in a state of fusion; the non-oxygenated oil then passes over pure. (Gerhardt & Cahours, *N. Ann. Chim. Phys.* 1, 61.)

If a volatile oil has been partly converted into a resin by continued

exposure to the air, it may be freed from the resin by distillation with water.—Any moisture which adheres to an oil may be removed by continued contact and agitation with chloride of calcium, and subsequent decantation.

Adulteration of Volatile Oils proper.

I. *With Fixed Oils.* — 1. Oils thus adulterated leave upon paper a greasy spot, which remains even after long-continued warming at 100°.— 2. When the mixture is distilled with water, the volatile oil passes over, while the fixed oil remains, and may be detected by saponifying it with potash.—3. On dissolving the volatile oil in three times its volume of 80 per cent. alcohol, the greater part of the fixed oil remains undissolved.

II. *With Alcohol.* — 1. When the proportion of alcohol is large, the greater part of it may be extracted by water, the liquid acquiring a milky turbidity. Hence the quantity of alcohol may be determined by shaking up the oil with an equal bulk of water in a graduated test-tube four inches long, and observing the diminution of volume. (Lipowitz, *N. Br. Arch.* 29, 932.) The result, however, is not quite accurate, because the separated oil still retains a portion of alcohol. — 2. A mixture of 5 parts of oil of turpentine and 1 part of alcohol, does not become turbid on addition of water, and requires frequent agitation with fresh quantities of water to free it from the greater part of the alcohol. When poured upon water, it may be observed to give up the alcohol in striæ. (Vauquelin, *Ann. Chim. Phys.* 19, 279; also *Schw.* 35, 438.) — 3. The mixture, when distilled with water, gives off the alcohol at the very beginning of the distillation; and this first distillate, when concentrated by rectification, yields alcohol, easily recognized by its smell, taste, density, boiling point, and flame. — 4. Into a graduated tube, two-thirds filled with the oil, some pieces of chloride of calcium, free from dust, are introduced, and the whole heated for five minutes on the water-bath, with frequent agitation. If no alcohol is present, the lumps of chloride of calcium appear unaltered after cooling; if a small quantity is present, they appear effloresced and baked together; and a larger quantity causes them to deliquesce with the alcohol into a fluid layer, the oil floating on the top, and appearing diminished in volume in proportion to the quantity of alcohol present. It is best to introduce only a small quantity of chloride of calcium at first, so that, if the quantity of alcohol should be but small, the alterations in the chloride of calcium may still be perceptible. (Borsarelli, *J. Pharm.* 26, 1, 29.) A mixture of 480 grains of oil of lemons and 15 grains of alcohol thus treated, converts 3 grains of chloride of calcium into a liquid. (Brandes, *N. Br. Arch.* 24, 113.) From some oils, however, as from oil of mustard, alcohol is not easily separated by chloride of calcium. (Lipowitz.) — 5. Oil containing alcohol takes up small quantities of water without turbidity when agitated with that liquid. (Herzog, *N. Br. Arch.* 28, 16.)—6. Potassium oxidizes in the oil, with evolution of gas, the more quickly, as the quantity of alcohol present is greater. A piece of potassium as large as the *Semen Psyllii* should remain unaltered for five minutes in a drop of pure oil; with $\frac{1}{25}$ of alcohol, it disappears in less than five minutes; with $\frac{1}{4}$, in less than a minute; in which case it runs about like a shining fused metallic globule till it is oxidized. (Béral, *J. chim. méd.* 3, 381; also *Berl. Jahrb.* 29, 2, 185.) By this method, $\frac{1}{4}$ alcohol may be

detected with certainty, $\frac{1}{12}$ with less certainty, $\frac{1}{16}$ but uncertainly; if the alcohol amounts to $\frac{1}{12}$ or less, the potassium does not fuse into a globule, but still produces a stronger evolution of gas than in pure oil. The oxidation of the potassium may likewise proceed from water instead of alcohol in the oil. (Pleischl, *Zeitschr. Phys. v. W.* 2, 308; Lipowitz.) Doubtless also, the difference of rapidity with which the potassium is oxidized, varies with the nature of the oil, the oxidation being more rapid when the oil contains oxygen. — 7. A pure volatile oil agitated with an equal volume of olive-oil, yields a clear mixture; whereas that which contains alcohol forms a turbid mixture, the alcohol being separated. (Righini, *J. chim. méd.* 20, 351.)

III. *Adulterations of expensive Oils with Oil of Turpentine.*—1. The presence of this adulteration may be detected by the smell, especially on rubbing the oil between the hands, or after setting it on fire and then blowing it out.—2. Since oil of turpentine is less soluble in hydrated alcohol than many other oils, the suspected oil may be agitated with its own bulk of 80 per cent. alcohol; if oil of turpentine, anise, or fennel, be present, the solution is incomplete.—3. Oil of turpentine mixes much less easily with fixed oils, than the oils of marjoram, lavender, valerian, sage, peppermint, or wormwood. If, therefore, 3 grammes of the suspected oil be agitated with 3 grammes of poppy-oil, and the mixture remains turbid, we may conclude that the oil is not mixed with turpentine; for even a small quantity of the latter would render the mixture clear. This method is not applicable to the oils of thyme and rosemary. (Mero, *J. chim. méd.* 21, 93.) — 4. Many volatile oils dissolve the colouring matter of sandal-wood, but oil of turpentine does not; the presence of the latter will, therefore, diminish the solvent power of the other oil. (Voget, *Ann. Pharm.* 6, 42.) — 5. Oil of turpentine becomes strongly heated, and detonates by contact with iodine; many other oils do not; but if the latter are mixed with only a small quantity of oil of turpentine, they likewise detonate by contact with iodine. (Tuchen.)

Those volatile oils which are free from oxygen are specifically the lightest; their density ranges from 0·627 (the most volatile oil of oil-gas) to 0·921 (heveene); the specific gravity of non-oxygenated camphors varies from 0·870 (paraffin) to 1·048 (naphthalin). Oxygenated volatile oils and camphors vary in density from 0·800 to 1·100.—The solidifying point of volatile oils in general is in some cases below 0°,—sometimes being very low and therefore unknown,—such oils being the volatile oils properly so called;—in other cases, that is to say, in the camphors or stearoptenes, it is above 0°, and among these, phenene melts at + 6°, chrysene not till heated to 240°. In the solid state, volatile oils (taking the term in its more general sense) are crystalline: in the liquid state, they have a thin oily consistence. They are colourless; any yellowish or brownish tint that they may exhibit being due to admixture of resin. The oils of certain *Compositæ* are, however, coloured blue or green, probably from admixture of a volatile blue colouring matter.—Volatile oils have great refracting power.—The boiling points of non-oxygenated volatile oils are given in the table on pages 154, 155, whence it appears that they vary between −10° (the most volatile oil of oil-gas) and 260° (oil of copaiba), and in camphors, between 86° (phenene) and 380° (paraffin). The boiling points of oxygenated oils are comparatively higher, as may be seen by some examples in the table just cited. Most volatile oils, properly so called, boil between 150° and 200°; oil of copaiba at 260°,

and several camphors between 300° and 400°. At these temperatures, provided the air be excluded (which might otherwise convert part of the oil into resin), the non-oxygenated oils distil over unchanged; those which contain oxygen, having higher boiling points, are liable to partial decomposition when distilled at those temperatures.

The volatile compounds belonging to this class are distinguished by a powerful odour, sometimes pleasant, sometimes repulsive, and form the odoriferous principles of many parts of plants and some parts of animals.—Some volatile oils are tasteless; others have a fiery aromatic flavour; others, again, an acrid taste, and these latter have likewise an acrid action on the animal body.

According to Liebig (*Chim. org.* 2, 308), volatile oils appear to emit a stronger odour in proportion as they oxidize more quickly in the air. When volatile oils free from oxygen, such as the oils of turpentine, elder, and lemon, are distilled over freshly burnt lime in an apparatus exhausted of air or filled with carbonic acid gas, they can scarcely be distinguished by their odour; but by exposing them for a while to the air, and more especially by saturating paper with them, the characteristic odours are restored.

Volatile oils appear to be incapable of emitting any odour, except in presence of moisture. Paper moistened with a volatile oil, and then perfectly dried, no longer emits any odour; but the odour becomes apparent on exposing the paper to the air, or more quickly by moistening it with a few drops of water. *Flores Rosarum*, *Sambuci*, or *Verbasci*, likewise completely lose their odour when thoroughly dried, but recover it on exposure to damp air. (J. A. Buchner, *Repert.* 15, 57.)—When violets are dried under a bell jar containing chloride of calcium, they retain their blue colour, but completely lose their smell, which, however, is entirely restored by moistening them with water. (Hünefeld, *J. pr. Chem.* 7, 235.)

The cold infusion of roses, orange-blossom, lime-blossom, or elder-blossom, acquires a much stronger odour on addition of sulphuric acid; this acid likewise imparts characteristic odours to the inodorous decoction of gall-nuts, horse-chestnuts, barley, and yellow and red sandal-wood. A much more strongly smelling water is also obtained by distilling roses (as was long ago recommended by Albertus Magnus), elder-blossom, lime-blossom, or pinks, with a mixture of water and sulphuric acid, than by distilling them with water alone. Volatile oils may be completely deprived of their odour and fiery taste, by proper treatment with caustic alkalis and by other means. They may, therefore, be regarded as compounds of inodorous oils with acids, to which the odour and burning taste of the entire oil are properly due. Many volatile oils yield two acids, one liquid and the other crystalline. (Couerbe, *J. Pharm.* 15, 598; 19, 542; the latter also in *Pogg.* 31, 525.)—Couerbe has not hitherto fulfilled his promise of confirming this view by more exact observations, and thereby removing the doubts which attach to it.

The more important *Decompositions* or *Reactions* of Volatile Oils are as follows:

1. Those oils which have a high boiling point are partly decomposed by distillation, *per se*, and leave a residue of charcoal; but when distilled with water or gently heated in the air, they may be volatilized without decomposition. But even the more volatile oils, when mixed with earthy

substances, such as clay, chalk, sand, &c., which mechanically prevent their volatilization, are partially decomposed by distillation, combustible gases being evolved, and charcoal left behind; if they contain oxygen, they may likewise yield carbonic oxide, acetic acid, &c. When the vapour of a volatile oil is passed through a red-hot tube, it is resolved into combustible gases and charcoal, which is sometimes finely divided, sometimes shining, dense, and difficult to burn; the portion of the oil which has passed over undecomposed, is often found to be altered in its properties, as, for example, in its boiling point.—2. Volatile oils are very inflammable, and burn with a clear flame which deposits a large quantity of soot. If the vapour of a volatile oil be made to issue from a fine jet, under a pressure of 1—6 centimetres of mercury, it does not take fire till it has reached a distance of some centimetres from the jet; that is to say, till it has become mixed with 4 or 5 times its volume of air; it then burns with a bright flame, which no longer smokes, and may be used for illumination. (Busson-Dumaurier & Ronn, *Compt. rend.* 16, 1164.)—Volatile oils may be used like alcohol to feed the lamp without flame. (Karmarsch, *Gilb.* 75, 83.) The oils of amber, anise, juniper, savine, rosemary, peppermint, wild marjoram, nutmeg, cinnamon, and cloves, emit acid vapours when burnt in this manner. (Miller, *Ann. Phil.* 28, 21.) A piece of red-hot spongy platinum, laid upon common camphor, continues to glow, and sinks deeply into the camphor. (Gm.).—3. Volatile oils proper, when placed in vessels not perfectly closed, and at the medium temperature of the air, absorb oxygen-gas; acquire the power of reddening litmus strongly, from formation of benzoic, cinnamic, acetic, and other organic acids; and are then partially converted into resins, becoming viscid and less odoriferous, and passing from the colourless state to yellow or red-brown, or from blue to brown. Oils thus altered are resolved by distillation into pure oil and a residue of resin. The absorption of oxygen takes place with different degrees of rapidity in different oils. For the first few days it goes on slowly, then increases in rapidity up to a certain limit, beyond which it again diminishes, and after several months becomes imperceptible. During this change, and especially towards the end, the oil exhales a small quantity of carbonic acid, and a still smaller quantity of hydrogen. At the same time, a small quantity of very acid water is produced, which is loosely attached to the resinized oil, but may be separated from it either by the application of heat or by exposure to the sun. Rock-oil absorbs scarcely any oxygen, and therefore forms neither acids nor resin. (Th. Saussure.)—The formation of acid and water was observed by Fourcroy.—The oils of *Valeriana off.*, *Artemisia Absinthium*, *Carum Carvi*, *Juniperus communis*, *Citrus Aurantium* and *medica*, *Melissa off.*, *Dracocephalum Moldavica*, *Mentha piperita* and *crispa*, *Origanum vulgare* and *Majorana*, *Salvia off.* and *Laurus Cinnamomum*, *Cassia*, and *Sassafras*, are neutral when fresh, but after exposure to the air in thin layers, for intervals varying from a few days to several months, acquire an acid reaction, in consequence of the formation of a crystalline acid, the oil still remaining fluid. They then thicken in consequence of the formation of resin and acetic acid, which latter is given off with a pungent odour, and if the oil be enclosed in a confined portion of air over hydrate of potash, converts that alkali into an acetate, carbonate of potash being at the same time produced from carbonic acid given off by the oil. The oils of camomile, anise, fennel, roses, and turpentine, on the other hand, acquire no acid reaction at first, not indeed till they begin to assume the resinous condition, and acetic

acid begins to form. (Bizio.)—The crystalline acid often formed in abundance from volatile oils at the commencement of the oxidation, varies according to the nature of the oil; in some cases, it has been found to be benzoic acid; in others, cinnamic.—When oxygen gas is passed through a volatile oil, a formation of acid likewise takes place at first, most quickly when the oil is suspended in water; the aqueous solutions of the oils likewise turn sour on exposure to the air.—According to Unverdorben (*Pogg.* 8, 483), volatile oils, when they thicken in the air, are converted: (1) into a difficultly volatile oil having but little odour; (2) into a resin soluble in potash; (3) into a resin insoluble in potash; (4) into an oily acid, insoluble in water, lighter than water, and having a sweet, pungent taste. The same products are obtained, but in larger quantity, by passing volatile oils through a red-hot tube. The thickening takes place with various degrees of rapidity, according to the nature of the oil.—4. A similar decomposition to that which takes place in the air, is likewise produced, by placing the oil in contact with nitrous gas, which it rapidly absorbs (Priestley); also by boiling the oil with oxide of copper or peroxide of lead, water being then formed (A. Vogel); or by digesting it with mercuric nitrate or corrosive sublimate, these bodies being thereby converted into mercurous nitrate and calomel respectively. (Margueron.) Volatile oils are likewise resinized by bichloride of tin and pentachloride of antimony, the latter often yielding reduced metal. Oils which easily resinize in the air are likewise immediately thickened by agitation with a warm concentrated solution of tersulphate of ferric oxide. (Berzelius.)—5. Volatile oils absorb chlorine gas, with evolution of heat, and are converted into viscid substances. (Thénard.) Hydrochloric acid is frequently formed in this reaction, a substitution of chlorine for hydrogen likewise taking place. Bromine exhibits similar reactions. (Laurent.)—6. Many volatile oils proper give up their hydrogen to iodine so rapidly, and with so great a development of heat, that an explosion takes place accompanied with evolution of violet and yellow vapours. This is the case with the oils of turpentine, juniper, savine, lemon, rosemary, and lavender. The residue is a thickened oil or a brown acid resin. These oils lose by age the property of deflagrating with iodine.—Other oils dissolve iodine quickly with or without evolution of heat, forming therewith a brown, thickish oil, or a soft or hard resin, with separation of a brown liquid, containing hydriodic acid. Such is the case with *Oleum Cinnamomi*, *Sassafras*, *Caryophyllorum*, *Rutæ*, *Tanaceti*, *Carvi*, *Fœniculi*, *Menthæ piperitæ* and *crispæ*, and the *Oleum animale Dippelii*. (Tuchen, Walcker, Flashoff, Zeller, Winckler)—¶ When oil of anise or fennel is dropped into a cold saturated solution of iodine in aqueous iodide of potassium, a gelatinous magma is formed, which, on addition of six or eight times its volume of alcohol, deposits a pulverulent substance, becoming dazzling white after washing with alcohol. This body is free from iodine, and appears to be composed of $C^{30}H^{18}O^4$. It may be supposed to be formed by the addition of 1 At. O to 3 At. of anise or fennel-camphor:

$$3C^{10}H^8O + O = C^{30}H^{18}O^4.$$

The oils of cumin, wormwood, camomile, tansey, rue, cloves, and peppermint, do not yield any similar product when thus treated. (Will, *Ann. Pharm.* 65, 230.) ¶—7. Fuming nitric acid decomposes volatile oils proper, mostly with great rapidity, the action being attended with evolution of gas, and with development of heat often amounting to the most vivid

inflammation; those volatile oils which are not set on fire by fuming nitric acid, generally burst into flame when treated with nitric acid to which half its bulk of sulphuric acid has been added. After the combustion, a residue of charcoal is left. If, however, the oil does not take fire, there remains a soft, bitter resin, which retains hyponitric acid, even after long washing with water, and a yellow or brown acid liquid from which water still separates a resinous substance. Camphors are not so rapidly decomposed; several of them and of other volatile oils are converted by heating with dilute nitric acid, partly into peculiar acids (benzoic and anisic acids), partly into oxalic acid. Many oils turn yellow when mixed with $\frac{1}{4}$—$\frac{1}{2}$ concentrated nitric acid; others first turn pale red, then bright red, and after 24 hours, brown; others, again, acquire a beautiful violet colour. (Bonastre, *J. Pharm.* 15, 663.)—Oil of vitriol mixes with most volatile oils proper, causing rise of temperature and evolution of sulphurous acid, together with a volatile oil (probably eupione) which smells of strawberries; the product is a thick brown liquid, from which water, in many cases, separates an isomeric compound (*e. g.*, anisoin from anise-oil); in other cases, a brown acid substance, which behaves, sometimes like artificial tannin, sometimes like an acid resin, dissolves in alcohol and alkalis, and, to a certain extent, also in water; heating the sulphuric acid solution causes the mass to carbonize. Camphors, which usually dissolve without decomposition in cold oil of vitriol, likewise become charred when heated with it.—Certain non-oxygenated volatile oils, such as eupione and paraffin, do not mix with cold oil of vitriol, or undergo any alteration by contact with it. Respecting the peculiar colouring of different oils by cold oil of vitriol, *vid.* Gaultier de Claubry. (*J. Phys.* 81, 69.)—9. Oils consisting wholly of carbon and hydrogen are not acted upon in any way by potassium or potash.

Combinations.—A. Volatile oils proper and many camphors are slightly soluble in water to the extent of about 1 pt. in 1000; those which contain oxygen dissolve more freely than those which do not. The solution is sometimes obtained by agitating the volatile oil with water, but more frequently by distilling the water with substances which contain the volatile oil. The products are called *Distilled Waters* (*Aquæ distillatæ*). They are transparent and colourless, unless the oil is in excess, in which case it remains for a long time suspended in the liquid and renders it turbid; they possess the taste and smell of the volatile oils which they contain. Agitation with a fixed oil (Davies, *J. Pharm.* 9, 16), or with ether, withdraws the volatile oil from the water, and on evaporating the ethereal solution, the greater part of the oil is left behind. (Soubeiran, *J. Pharm.* 17, 620; 19, 50.) Agitating the water with common salt, separates a considerable portion of the oil; such is the case with *Aqua Fœniculi*, *Menthæ piperitæ*, and *Cinnamomi*, and with water containing primrose-camphor. (Hünefeld, *J. pr. Chem.* 9, 24.)

To determine the quantity of volatile oil contained in a distilled water, half an ounce of the liquid is to be mixed with a small quantity of gelatinous starch, and a solution of 1 grain of iodine in 500 grains of alcohol and 1500 grains of water added, with agitation, till the oil ceases to give up hydrogen to the iodine, and consequently the iodine begins to impart a blue colour to the starch. It must, however, be observed, that different oils destroy the blueing properties of different quantities of iodine; thus, the same quantity of iodine is required to impart an incipient blueness to 24 ounces of water mixed with starch paste,

when the water contains 0·5 grain of oil of roses, 2·6 gr. fennel-oil; 3·6 gr. oil of *Mentha crispa*, 5·3 gr. peppermint-oil, or 20 gr. oil of cinnamon. Hence oil of roses gives up nearly 40 times as much hydrogen to the iodine as an equal quantity of oil of cinnamon. (Gruner, *Jahrb. prakt. Pharm.* 7, 304.)

The oil contained in the water gradually changes into acid and resin, when exposed to the air, especially in a warm place; it is also immediately precipitated as a resinous matter by chlorine. A distilled water may be kept unaltered for a long time in a cellar at a temperature of 10° or 12°; but at 25° or 30° it turns acid in a week, especially if exposed to the sun; by this change, however, the water loses little or nothing of its peculiar odour. The water which acidifies most quickly and strongly of all is *Aqua Melissæ*, then come *Aqua Rosarum*, *Sambuci* and *Chamomillæ*, while *Aqua Hyssopi* and *Menthæ crispæ* and *piperitæ* remain unaltered. (Flashoff, *N. Tr.* 11, 1, 294; *Br. Arch.* 21, 222.)—If the distilled water contains a small quantity of alcohol, a considerable quantity of acetic acid is quickly formed in it. (Warington, *Phil. Mag. J.* 26, 574.)

Many distilled waters, when kept in well closed bottles, become slimy, lose their proper odour, and acquire an offensive smell, whereas, if kept in loosely covered vessels, they remain unaltered. This change appears to arise from the action of mucous and albuminous particles carried over in the distillation, which, when they putrefy, rob the volatile oil of a portion of its oxygen, or give up to it a portion of their own hydrogen, thereby depriving it of its peculiar odour; hence such waters recover their odour on exposure to the air.—The same raspberry-water spoils in four weeks if kept in a bottle of colourless glass, but may be kept unaltered for a year in a bottle of orange-coloured glass: a proof of the influence of light. (Hänle, *Repert.* 67, 392.)—The white flakes deposited from distilled waters consist of plants. (Simonin.) The white or brown mucus thus separated does not dissolve either in alcohol or in boiling potash, and, when examined with a lens, appears like an agglomeration of fine confervoidal fibres resembling mother of vinegar. (Gruner.) According to Buchner (*Br. Arch.* 7, 284), *Aqua Rosarum*, *Menthæ piperitæ*, *Cinnamomi*, keep best in close vessels; *Aqua Chamomillæ*, *Fœniculi*, *Naphæ*, *Menthæ crispæ*, *Hyssopi*, *Cerasorum*, less perfectly; and *Aqua Valerianæ*, *Rutæ*, *Sambuci*, *Tiliæ*, *Rubi Idæi*, *Petroselini*, *Melissæ*, *Salviæ*, worst of all; but if such waters be once distilled as long as water containing oil passes over, a distillate is obtained which may be kept without alteration in close vessels for four years or more.—A good mode of preservation is to leave the distilled water for several days in contact with the oil which has passed over, agitating frequently; then filter it into medicine-glasses containing from half a pound to a pound, bind the glasses round with moist bladder, introduce them, according to Appert's method (p. 100), into water heated to ebullition in a boiler, and bind round the bladders, after cooling, with paper. Even raspberry-water thus treated may be kept unaltered for 8 years. (Wend, *Jahrb. prakt. Pharm.* 1, 35.)

Certain hydrocarbons, oil of turpentine for example, when kept over water, take up the elements of water, and are converted into camphors.

B. Liquid volatile oils absorb small quantities of carbonic oxide, carbonic acid, and nitrous oxide gas, and larger quantities of sulphurous acid, hydrosulphuric acid, or fluoride of silicium.

With the aid of heat, they dissolve a tolerably large quantity of

phosphorus, forming a liquid which shines in the dark, and deposits the greater part of the phosphorus on cooling.

They also, when heated, dissolve a small quantity of *sulphur*, which crystallizes out again on cooling; when boiled for some time with sulphur, they unite in the decomposed state, with considerable quantities of that substance, forming a brown, greasy, stinking mass, called *Volatile Balsam of Sulphur*, which, if heated for a longer time, quickly evolves a large quantity of sulphuretted hydrogen gas. — Most camphors may also be made to unite with sulphur and phosphorus by fusion.

Bisulphide of Carbon mixes in all proportions with liquid oils, and dissolves camphors.

C. Many volatile oils and camphors absorb large quantities of *hydrochloric acid gas*, producing great rise of temperature, and forming sometimes oily, sometimes camphoroidal compounds, in which the chlorine cannot be detected by nitrate of silver.—With *hydrobromic acid gas* they behave in a similar manner.—Many of them combine with chloride of phosphorus and chloride of sulphur, the combination being attended with evolution of heat.

D. Only a few oils, which contain oxygen, and have a slightly acid character, viz., creosote, oil of cloves, and oil of pimento, absorb *ammoniacal gas* in abundance, dissolve in aqueous alkalis, and form with these and other bases, saline compounds, in which the odour of the oil is destroyed.

Volatile oils dissolve *oxide of copper* at ordinary temperatures, but reduce it on application of heat (A. Vogel); they dissolve *protoxide of lead* with facility (Schweitzer); mix with *chloride* and *fluoride of arsenic;* and abstract *corrosive sublimate* from its aqueous solution, whereby they become thick and solid. They also separate *chloride of gold* from its aqueous solution; and on subsequent exposure to light, the gold is set free in the metallic state.

E. Volatile oils mix readily with *Hydrocyanic acid*, abstract that acid from water, and form a mixture which does not readily decompose, and is specifically heavier than water. (Ittner.) They absorb a few volumes of *Cyanogen gas*, and dissolve *Iodide of Cyanogen* with facility.

F. Many volatile oils and camphors are capable of mixing with certain *organic acids*, such as acetic, succinic, benzoic, camphoric, suberic acid, and the fatty acids. Strong acetic acid dissolves many volatile oils and camphors. (Fourcroy & Vauquelin, *Scher. J*, 5, 282; Vauquelin, *Ann. Chim. Phys.* 19, 279.) Acetic acid, which holds volatile oils in solution, reduces mercurous nitrate or silver-nitrate at a boiling heat, but not so quickly as formic acid. (Walcker.)

G. Volatile oils dissolve readily in alcohol, and most of them mix with absolute alcohol in all proportions. According to Saussure, the solubility of different oils increases with the quantity of oxygen which they contain; hence also the same oil is more readily soluble, the longer it has been exposed to the air. Such solutions are obtained by distilling parts of plants which contain the volatile oil with alcohol and a small quantity of water, which prevents charring towards the end of the distillation. Many of the preparations which apothecaries call *Spirits* are solutions of this kind, as also are *perfumed waters*, such as *Eau de Cologne*,

Lavender-water, &c. Most camphors also dissolve readily in alcohol; there are but few which dissolve with difficulty. All these solutions burn with a bright flame, which is smoky if the solution contains much oil. When mixed with water, they turn milky, from separation of the oil, part of which, however, remains dissolved in the aqueous mixture. If a volatile oil is mixed with only a small quantity of alcohol, it does not become turbid when mixed with water, and only gives up its alcohol when repeatedly agitated with fresh quantities of water.

Wood-spirit and *Acetone* behave like alcohol; so likewise do *Ether* and several other ethereal liquids, excepting that from the latter the oils cannot be separated by water.

Volatile oils mix with *Fats*, dissolve most Resins and *Resinous Colouring matters*, and several organic bases; they also mix with one another.

b. Derivative or Secondary Nuclei.

In secondary nuclei, the H-atoms of the primary nucleus are replaced wholly or partially by an equal number of atoms of O, S, I, Br, Cl, N, Ad, X, Cy, or SO^2. Several of these elements may enter at the same time into the same secondary nucleus, so that it may contain three other substances in addition to the carbon. Many secondary nuclei are not known in the separate state, but are merely hypothetical substances, from which the composition of other compounds may be most conveniently deduced.

The following are examples of secondary nuclei which are known to exist in the free state:

1. *Arranged according to the Primary Nuclei.*

Methylene or Palene=C^2H^2, gives C^2HCl; C^2NH.

Ethene or Ethylene=C^4H^4, gives C^4H^3Cl; $C^4H^2Cl^2$; C^4HCl^3; C^4Cl^4; C^4H^3Br; Cr^4Br^4; C^4H^3I.

Butyrene=C^8H^8, gives C^8H^7Cl.

Phenene or Phenylene=$C^{12}H^6$, gives $C^{12}H^3Cl^3$; $C^{12}H^3Br^3$; $C^{12}H^5N$; $C^{12}H^5X$; $C^{12}H^4XAd$.

Toluol=$C^{14}H^8$, gives $C^{14}H^7Cl$; $C^{14}H^2Cl^6$; $C^{14}H^6X^2$.

Styrol=$C^{16}H^8$, gives $C^{16}H^7X$; $C^{16}H^7Cl$. Indigo-blue=$C^{16}H^5NO^2$, probably also belongs to this head.

Naphthalin=$C^{20}H^8$, gives the secondary nuclei mentioned on page 20, besides several others.

To Cymene or Cymol=$C^{20}H^{14}$, appear to belong, $C^{20}H^{12}O^2$; $C^{20}H^9Cl^3O^2$; $C^{20}H^{10}X^2O^2$, &c.

2. *Arranged according to the nature of the substances which replace the hydrogen.*

Oxygen-nuclei: Parasalicyl, $C^{14}H^5O^3$ (from $C^{14}H^8$); — Suberone, $C^{16}H^{14}O^2$ (from $C^{16}H^{15}$);—common camphor, $C^{20}H^{16}O^2$ (from $C^{20}H^{18}$);—Anise-camphor, $C^{20}H^{12}O^2$ (from $C^{20}H^{14}$);—$C^{20}H^7O$ from $C^{20}H^8$. — Many kinds of sugar probably belong to this class; *e. g.*, Grape-sugar, $C^{12}H^{12}O^{12}$, common sugar, $C^{12}H^{11}O^{11}$, and Milk-sugar, $C^{12}H^{10}O^{10}$; the number of the C-atoms in the unknown primary nuclei, would be to that of the

hydrogen atoms as 12:24; 12:22; and 12:20 (or, 24:48; 24:44, and 24:40); perhaps, however, these sugars are compounds of nuclei with different quantities of HO.

Sulphur-nucleus: Oil of garlick, C^6H^6S (perhaps derived from the unknown primary nucleus C^6H^6).

Iodine-, Bromine-, and *Chlorine-nuclei:* C^2Br^2;—C^4H^3I; C^4H^3Br; C^4Cl^4; $C^4H^2Cl^2$;—C^8H^7Cl;—$C^{12}H^3Br^3$;—$C^{14}H^7Cl$; $C^{14}H^6Cl^2$;—$C^{28}H^{11}Cl$;—$C^{20}H^7Br$; $C^{20}H^6Cl^2$; $C^{20}H^4Cl^4$; $C^{20}H^4Br^2Cl^2$; $C^{20}H^2Cl^6$; $C^{20}Cl^8$;—$C^{20}H^9Cl^3O^2$ (from $C^{20}H^{14}$);—$C^{20}H^{17}Cl$; $C^{20}H^{12}Cl^5$; $C^3H^{15}ClO^3$ and $C^{20}H^{10}Cl^6O^3$ (from $C^{20}H^{16}$).

Azo-nuclei: The following compounds probably belong to this class: Hydrocyanic acid, C^2NH;—Mellon, C^6N^4;—Oil of Mustard, $C^8H^5NS^2$ (8:8); but other formulæ are more probable.—Indigo-blue, $C^{16}H^5NO^2$ (16:8);—Pyrobenzile, $C^{42}H^{16}N^2$ (42:18);—*Azotide benzoilique,* $C^{28}H^{10}N^2$ (28:12).

Amidogen-nuclei: To this class probably belong: Bisuccinamide, $C^8H^3AdO^4$ (8:8);— Phthalimide, $C^{16}H^3AdO^4$ (16:8); — Imabenzyl, $C^{28}H^9AdO^4$ (28:12).

Nitro-nuclei: These compounds are generally formed by treating a primary nucleus with concentrated nitric acid (p. 73). The following are examples: Nitrobenzide, $C^{12}H^5X$, and Binitrobenzide, $C^{12}H^4X^2$ (12:6);—Nitrotoluide, $C^{14}H^7X$, and Binitrotoluide, $C^{14}H^6X^2$ (14:8);—Nitrostyrole, $C^{16}H^7X$ (16:8).—In a similar manner, from Stilbene, $C^{28}H^{12}$, are formed the nitro-nuclei, $C^{28}H^{11}X$ and $C^{28}H^{10}X^2$, and from Naphthaline, $C^{20}H^8$, the nitro-nuclei, $C^{20}H^7X$, $C^{20}H^6X^2$, $C^{20}H^5X^3$, and $C^{20}H^4XCl^3$.

Sulphobenzide, $C^{12}H^5(SO^2)$, is a sulphurous acid nucleus, formed from Benzol$=C^{12}H^6$.

Probably, also, there exist nuclei, in which H is replaced by cyanogen $=C^2N=Cy$, or by sulphocyanogen $=CyS^2$. Thus, Oil of Mustard, $C^8H^5NS^2$, may be regarded as C^6H^5Cy,S^2, or as $C^6H^5CyS^2$.

B. Combinations of a Primary or Secondary Nucleus with Substances externally attached to it.

Envelope-nuclei.

a. Compounds with Hydrogen.

α. Nuclei combined with 1 *At. Hydrogen.*

Indigo-blue, $C^{16}H^5NO^2$, is converted by hydrogenizing agents into indigo-white, $C^{16}H^5NO^2,H$. Many other vegetable colouring matters are converted, under similar circumstances, into colourless compounds, probably also by taking up 1 At. H. Indigo-white has the characters of a weak acid, so that perhaps the compounds of certain nuclei with 1 At. H should be regarded as hydrogen-acids. This 1 At. H appears to be always very loosely combined with the nucleus.

To avoid uneven numbers of atoms, Laurent & Gerhardt double the atom, writing, for example, indigo-white as $C^{32}H^{10}N^2O^4,H^2$.

¶ *Alcohol-radicals.*—These bodies contain odd numbers of hydrogen-atoms, and may, therefore, be regarded, empirically at least, as compounds of nuclei with 1 At. hydrogen: *e. g.,* Methyl$=C^2H^3=C^2H^2,H$;

Ethyl=C^4H^5=C^4H^4,H, &c. A few of them, viz., Methyl, Ethyl, Butyl =C^8H^9, Amyl=$C^{10}H^{11}$, and Caprotyl=$C^{12}H^{13}$, have lately been obtained in the separate state. The methods by which their isolation has been effected are as follows:

1. By the action of zinc or potassium on the iodides or cyanides of the radicals. (Frankland & Kolbe.) Iodide of ethyl, strongly heated with finely divided zinc in a closed tube, yields ethyl and iodide of zinc, part of the ethyl being however decomposed into olefiant gas and hydride of ethyl, C^4H^5,H; thus:

$$2C^4H^5 = C^4H^4 + C^4H^5,H;$$

and another portion combining with part of the zinc, and forming the metalloidal radical, zinc-ethyl, C^4H^5Zn. If water be present, the whole of the ethyl is converted into hydride, thus:

$$C^4H^5I + HO + 2Zn = C^4H^5,H + ZnI,ZnO.$$

Similarly, if alcohol be present instead of water:

$$C^4H^5I + C^4H^6O^2 + 2Zn = C^4H^5,H + C^4H^4O + ZnI,ZnO.$$

Potassium likewise decomposes cyanide of ethyl, but the whole of the liberated ethyl is decomposed as above into C^4H^4 and C^4H^6.—Methyl and amyl are in like manner obtained by the action of zinc on their iodides.

2. By the action of light on the iodides of the radicals. (Frankland.) This process has hitherto been tried only on the iodide of ethyl. It effects complete decomposition, provided some substance be present which can absorb the liberated iodine. Thus, when the iodide is introduced into an inverted glass globe previously filled with mercury, and exposed to the rays of the sun, the iodine combines with the mercury, and ethyl is separated in the form of gas. In this case also, if water be present, hydride of ethyl is formed.

3. By the electrolysis of acids of the series $(CH)^nO^4$. The general formula of this decomposition appears to be:

$$(CH)^nO^4 = C^{n-2}H^{n-1} + 2CO^2 + H.$$

In this manner acetic acid, $C^4H^4O^4$, yields methyl, C^2H^3; valerianic acid, $C^{10}H^{10}O^4$, yields butyl, C^8H^9 (Kolbe, *Chem. Soc. Qu. J.* 2, 157); caproic acid, $C^{12}H^{12}O^4$, yields amyl, $C^{10}H^{11}$; and œnanthylic acid, $C^{14}H^{14}O^4$, yields caprotyl, $C^{12}H^{13}$. (Brazier & Gossleth, *Chem. Soc. Qu. J.* 3, 210.)

Methyl and ethyl are gaseous at ordinary temperatures; butyl, amyl, and caprotyl are liquids, the first boiling at 108°, the second at 155°, and the third at 202°. They do not combine directly with any of the elementary bodies, such as oxygen or chlorine; and it has not hitherto been found possible to reproduce from them, by direct union, any of the compounds of the methyl-, ethyl-series, &c.

The constitution of these hydrocarbons has given rise to considerable discussion. The formulæ, C^2H^3, C^4H^5, &c., originally assigned to them by Frankland & Kolbe, represent their vapours as monatomic (or, according to the more usual mode of expression, the equivalents represented by these formulæ correspond to two volumes of vapour, pp. 52, 53, and 154). As this amount of condensation differs from that of most other organic compounds, which are diatomic (the equivalent corresponding to 4 volumes of vapour), it has been maintained by several chemists that

the preceding formulæ ought to be doubled, *e. g.*, that methyl should be C^4H^6, ethyl, C^8H^{10}, &c.

This duplication of the formulæ was first proposed by Gerhardt (*Compt. mensuels*, 1848, 19; 1850, 11), who pointed out that the so-called radicals by no means exhibit the chemical characters which might be looked for in bodies analogous to the metals, and that they should rather be regarded as homologues of marsh-gas.

Hofmann (*Chem. Soc. Qu. J.* 3, 121) has likewise maintained that the formulæ C^2H^3, &c. ought to be doubled, and that the compounds in question cannot really be true organic radicals; first, because they do not combine directly with any of the elementary bodies, or give rise in any other way to the reproduction of methyl-, ethyl-, or amyl-compounds.—Secondly, because their vapour-volumes are different from those of all other known hydrocarbons.—Thirdly, because, if Frankland & Kolbe's formulæ be true, the boiling points of these compounds will not agree with Kopp's law (p. 55); thus the boiling points of butyl, amyl, and caprotyl differ successively by 47°, an interval more than double of that which generally corresponds to a difference of C^2H^2 in bodies of the ethyl-, methyl-, amyl-series, &c.: now the duplication of the formulæ would remove this anomaly.—Fourthly, because the decomposition of the iodides of the alcohol-radicals by zinc, is not perfectly analogous to that of hydriodic or hydrochloric acid, inasmuch as, in the latter case, no compound of zinc and hydrogen is formed, analogous to zinc-ethyl.

To these objections Frankland has given an elaborate reply, maintaining that these bodies are perfectly analogous to hydrogen, only less strongly electropositive. He points out, however, that the hydrocarbons obtained by the processes above enumerated, must be divided into two classes,—those of the one class being the true radicals, and having the general formula C^nH^{n+1} (n an even number), *e. g.*, methyl $= C^2H^3$ —while those of the other class, which are isomeric with the first, and are the hydrides of the radicals, have the general formula $C^{2n}H^{2n+1},H$; *e. g.*, hydride of ethyl, $C^4H^5,H = C^4H^6$; the former he regards as monatomic, the latter as ½-atomic. Thus the gas obtained by the electrolysis of acetate of potash, and by the action of zinc on dry iodide of methyl, is the true methyl, C^2H^3; while that obtained by the action of zinc or of light on iodide of ethyl in presence of water, or by the action of potassium on iodide of ethyl (not anhydrous), is not methyl, but the hydride of ethyl, C^4H^5H. That these two bodies are really not identical, but only isomeric, is shown by their behaviour with chlorine (*vid. Methyl*).—To the objection founded on the inactive character of these hydrocarbons, Frankland replies that we are not justified in expecting all organic radicals to exhibit the active properties of cacodyl. For it must be remembered that the simple radicals, that is to say, the metals and hydrogen, exhibit great diversities in their combining tendencies, presenting indeed a regular gradation of properties, from potassium, on the one hand, to hydrogen, gold, platinum, iridium, and nitrogen on the other, the bodies at one extremity of the scale exhibiting the most energetic affinities, while those at the other extremity show but little tendency to combine directly with any other element. It is not therefore surprising that the compound radicals should present similar differences; and that some of them, as cacodyl and zinc-methyl, should take fire on mere exposure to the air, while others, viz., the alcohol-radicals, should exhibit even less combining tendency than hydrogen, and even

be found incapable of reproducing any of the compounds in the series of which they form the basis.—With regard to the vapour-volumes of these radicals, Frankland observes that though they certainly differ from those of most hydrocarbons, they agree with that of hydrogen, with which they are in every respect analogous, and which, in fact, may be regarded as the first term in the series of organic radicals, thus:

$$H + C^2H^2 = C^2H^3;\ C^2H^3 + C^2H^2 = C^4H^5,\ \&c.$$

With respect to the deviation of the boiling point from Kopp's law, he observes that this law is founded chiefly on the differences observed in the series of alcohols and fatty acids; but in bodies of more simple construction, viz., the oxides, iodides, and chlorides of the radicals, greater differences are found; and hence it may be reasonably expected that in the radicals, which are simplest of all, the boiling points of the successive terms will exhibit still greater differences.—Lastly, it is not to be expected that a compound of zinc and hydrogen should be obtained by the action of zinc on hydrochloric acid, inasmuch as such a compound, if formed, would be instantly decomposed by the excess of hydrochloric acid present.

On comparing these several arguments, it appears most probable that the bodies which Frankland calls methyl, ethyl, &c., are really the true radicals, and are strictly analogous to hydrogen in their chemical relations; but that in the free state, their vapour-volumes correspond with those of other hydrocarbons, and consequently that the formulæ assigned to them by Frankland ought to be doubled. The apparent contradiction here implied, is reconciled by the view adopted by Brodie and by Gerhardt, viz., that, in the free state, the molecules of these radicals (hydrogen included) are made up by the union of two elementary atoms. Brodie has shown (*Phil. Trans.* 1850, 798; abstr. *Chem. Soc. Qu. J.* 4, 194) that the separation of an elementary body, such as hydrogen, from any of its combinations, may be regarded as a chemical synthesis of the particles of the isolated element, similar in fact to that which takes place in the separation of a compound body. Thus, when hydride of copper, Cu^2H, is acted upon by hydrochloric acid, Cu^2Cl is formed and 2H set free:

$$Cu^2H + HCl = Cu^2Cl + H^2.$$

The reaction which here takes place is truly a double decomposition, perfectly analogous to that which we observe in the action of hydrochloric acid on dioxide of copper:

$$Cu^2O + HCl = Cu^2Cl + HO;$$

the 2 At. hydrogen in the former case combining together just like the O and H in the latter. Many other examples tending to establish the conclusion that all chemical reactions may be viewed as double decompositions, and that the isolation of an elementary body always involves a chemical synthesis of the atoms of that body, may be found in Brodie's paper above referred to.

Now, when zinc acts on iodide of ethyl in presence of water, the products are oxyiodide of zinc and hydride of ethyl; thus [C^4H^5=Et]:

$$\left(\begin{matrix} IEt & HO \\ Zn & Zn \end{matrix}\right) = ZnI,ZnO + EtH;$$

and the reaction which takes place when no water is present, the products being iodide of zinc and free ethyl, may be represented in a similar

manner; thus, substituting iodide of ethyl for water on the left-hand side of the above equation, we have,

$$\left(\begin{matrix}\mathrm{IEt} & \mathrm{EtI}\\ \mathrm{Zn} & \mathrm{Zn}\end{matrix}\right) = 2\mathrm{ZnI} + \mathrm{Et}^2.$$

The action which zinc at high temperatures exerts upon water, may be regarded in a precisely similar manner, thus:

$$\left(\begin{matrix}\mathrm{OH} & \mathrm{HO}\\ \mathrm{Zn} & \mathrm{Zn}\end{matrix}\right) = 2\mathrm{ZnO} + \mathrm{H}^2.$$

In confirmation of these views, Brodie finds that zinc-ethyl and iodide of ethyl decompose each other when heated together to 170° in a sealed glass tube, forming ethyl and iodide of zinc, provided the action be assisted by the presence of a considerable quantity of ether, in which zinc-ethyl is soluble, thus:

$$\left(\begin{matrix}\mathrm{Et} & \mathrm{Zn}\\ \mathrm{Et} & \mathrm{I}\end{matrix}\right) = \mathrm{ZnI} + \mathrm{Et}^2.$$

It is highly probable that by similar methods, compound radicals, such as ethylo-methyl, ethylo-amyl, &c., may be formed.

According to this mode of viewing the composition of the radicals, ethyl stands to hydride of ethyl in the same relation as ether to alcohol, and would be to the compound radicals just alluded to, as ordinary ether to the compound ethers discovered by Williamson; thus:

$\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}$ Hydrogen.	$\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}^2$ Water.
$\left.\begin{matrix}\mathrm{C^4H^5}\\ \mathrm{H}\end{matrix}\right\}$ Hydride of ethyl.	$\left.\begin{matrix}\mathrm{C^4H^5}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}^2$ Alcohol.
$\left.\begin{matrix}\mathrm{C^4H^5}\\ \mathrm{C^4H^5}\end{matrix}\right\}$ Ethyl.	$\left.\begin{matrix}\mathrm{C^4H^5}\\ \mathrm{C^4H^5}\end{matrix}\right\}\mathrm{O}^2$ Ether.
$\left.\begin{matrix}\mathrm{C^4H^5}\\ \mathrm{C^2H^3}\end{matrix}\right\}$ Ethylo-methyl.	$\left.\begin{matrix}\mathrm{C^4H^5}\\ \mathrm{C^2H^3}\end{matrix}\right\}\mathrm{O}^2$ Ethylate of methyl.

According to this theory, the alcohol-radicals are strictly analogous to hydrogen in their mode of formation and their relations to other bodies; but in the free state, their vapours (that of hydrogen included) are ½-atomic, and the successive terms of the series, starting from hydrogen, differ, not by $\mathrm{C^2H^2}$, but by $2\mathrm{C^2H^2}$, which reconciles the apparent anomaly of the boiling points.

The same view is adopted by Gerhardt in his recent papers (*Comptes mensuels*, 1851, 169; *Ann. Pharm.* 83, 115), the formulæ being of course expressed according to his atomic weights (p. 27); thus:

$\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}$ Hydrogen.	$\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}$ Water.
$\left.\begin{matrix}\mathrm{C^2H^5}\\ \mathrm{H}\end{matrix}\right\}$ Hydride of Ethyl.	$\left.\begin{matrix}\mathrm{C^2H^5}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}$ Alcohol.
$\left.\begin{matrix}\mathrm{C^2H^5}\\ \mathrm{C^2H^5}\end{matrix}\right\}$ Ethyl.	$\left.\begin{matrix}\mathrm{C^2H^5}\\ \mathrm{C^2H^5}\end{matrix}\right\}\mathrm{O}$ Ether.
$\left.\begin{matrix}\mathrm{C^2H^5}\\ \mathrm{C\,H^3}\end{matrix}\right\}$ Ethylo-methyl.	$\left.\begin{matrix}\mathrm{C^2H^5}\\ \mathrm{C\,H^3}\end{matrix}\right\}$ Ethylate of methyl.

Comp. also Laurent (*Comptes mensuels*, 1850, 241); Wurtz (*N. J. Pharm.* 18, 230). ¶

β. *Nuclei combined with 2 At. Hydrogen.*

Marsh-gas, $\mathrm{C^2H^4}$, may be regarded as Methylene + 2H = $\mathrm{C^2H^2,H^2}$.—Paraffin, $\mathrm{C^{60}H^{60}}$, is probably = $\mathrm{C^{60}H^{48},H^2}$.—Similar formulæ may, perhaps,

be assigned to other hydrocarbons which may be obtained in the form of oils or camphors.—Glycerine, $C^6H^6O^6$, is perhaps $C^6H^6O^6,H^6$, and Mannite, $C^{12}H^{14}O^{12} = C^{12}H^{12}O^{12},H^2$; the last-mentioned compound may in fact be supposed to be formed from grape-sugar, $C^{12}H^{12}O^{12}$, in hydrogenising actions, such as processes of fermentation.

Lastly, the same type appears to include those organic compounds which possess more or less of the character of a salifiable base. These *Alkaloids* may be regarded as compounds of 2 At. hydrogen with a nucleus containing 1 or 2 At. nitrogen as such, and only in a few cases, as in the products of oil of mustard, in the form of amidogen. This nucleus, in addition to carbon and nitrogen, contains either hydrogen alone, or oxygen and sulphur in addition. Some few of these nuclei likewise contain part of the nitrogen in the form of amidogen or hyponitric acid. The nitrogen in the nucleus is essential; there is no alkaloid free from nitrogen. Among inorganic bases, ammonia exhibits the closest analogy to the alkaloids in its behaviour with acids and metallic salts; and as ammonia may be regarded as a compound of HN with H^3, so likewise may the alkaloids be regarded as compounds of a nucleus containing nitrogen with H^3. Moreover, as several atoms of oxygen united with nuclei form acids, and the strongest acids with nuclei free from nitrogen, so, on the other hand, it appears that 2H united with nitrogen-nuclei forms bases.

This view may be satisfactorily carried out with most of the compounds belonging to this type; but with regard to many, it is necessary to wait for a more complete determination of their composition; for the present it may be regarded as an attempt to explain the peculiar properties of the alkaloids from their peculiar composition (a nitrogen-nucleus and 2 At. hydrogen). Whatever probability, however, this theory may possess, we may be allowed to introduce in this place the consideration of alkaloids in general.

Alkaloids.

Organic Alkalis, Vegetable Alkalis, Organic Bases, Alkaloids, Bases végétales, Bases salifiables organiques.

Memoirs, which treat of several Alkaloids together:

Serullas.—Iodates and Chlorates of the Alkaloids. *Ann. Chim. Phys.* 45, 274.

Pelletier.—Action of Iodine. *Ann. Chim. Phys.* 63, 164; also *J. pr. Chem.* 11, 257.—Action of Chlorine. *J. Pharm.* 24, 153; also *J. pr. Chem.* 14, 180.

Regnault.—Composition. *Ann. Chim. Phys.* 68, 113; also *Ann. Pharm.* 26, 10.

Liebig.—Composition. *Ann. Pharm.* 26, 41.

A. v. Planta-Reichenau. *Reaction der Alkaloide.* Heidelb. 1846.

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The existence of organic *Acids* has long been recognised, but that of organic *Salifiable Bases* remained unknown until more recent times. Serturner first showed in 1806 (*A. Tr.* 14, 1, 37), and afterwards more completely in 1817 (*Gilb.* 55, 61), that morphine, which he had discovered in opium, behaved towards vegetable colours and acids like an alkali; and it was not till then that the basic nature of narcotine, a substance previously discovered in opium, and of cinchonine, obtained from Cinchona bark, was brought to light. This discovery led to the search for similar substances in many parts of plants distinguished by their poisonous or medicinal action, and to the discovery in many cases of an alkaloid existing

therein as the active principle, and generally in combination with an acid.

Many alkaloids may also be obtained by artificial processes. Unverdorben, in 1826, first discovered several volatile alkaloids as products of dry distillation; *e. g.*, Crystalline (Aniline), Odorine, &c. More recently, chemists have succeeded in preparing alkaloids artificially by other processes.

Preparation of Natural Alkaloids.

1. If the alkaloid is volatile without decomposition, the plant which contains it, or its concentrated aqueous extract, is distilled with a fixed alkali; the watery distillate, which generally contains ammonia as well as the alkaloid, is exactly neutralized with sulphuric acid; the liquid evaporated to dryness; the residue exhausted with absolute alcohol (or a mixture of it with ether), which dissolves the sulphate of the alkaloid, and leaves the sulphate of ammonia undissolved; the alcoholic solution evaporated to dryness, with frequent addition of water; and the residue distilled with a fixed alkali and water,—whereupon the alkaloid passes over, partly in the separate state, and partly dissolved in water. On agitating the aqueous solution with pure ether, decanting the ether from the watery liquid below it, and leaving it to evaporate, the alkaloid, whose boiling point is far below 100°, remains behind.

2. With the more fixed alkaloids, the following is the process generally adopted. The plant is exhausted with water, often with the addition of a small quantity of sulphuric, hydrochloric, or acetic acid; the brown colouring matter and other foreign substances, precipitated, if necessary, by acetate or subacetate of lead; the filtrate freed from lead by hydrosulphuric acid; and after sufficient concentration treated with ammonia, or a fixed alkali, or magnesia, in sufficient quantity to saturate the acid. By this process, the alkaloid, which is but very slightly soluble in water, is for the most part precipitated; but it generally requires to be purified by recrystallization from hot alcohol, or by digesting the acid or alcoholic solution with animal charcoal, &c.

For the separation of alkaloids, such as atropine, which are readily decomposed by alkalis, the cold concentrated aqueous extract is agitated with a fixed alkali and ether, or a mixture of ether and alcohol, and the ethereal solution of the alkaloid separated by decantation; when evaporated, it leaves the alkaloid in a state fit for further purification.

3. Since most alkaloids form with tannic acid a compound sparingly soluble in water, the extract of the plant prepared with hot water, or with water containing a very small quantity of sulphuric acid, may be neutralized, when quite cold, with ammonia, potash, or soda; the liquid mixed with a strong infusion of galls as long as a precipitate continues to form; and the precipitate collected on a linen cloth, washed with cold water, pressed to the consistence of dough, and then mixed with a slight excess of lime previously slaked to powder. The mixture, which becomes first green and afterwards brown, from decomposition of the tannic acid, is then dried over the water-bath, finely pulverized, exhausted by boiling with alcohol or ether, the solution filtered to separate the tannate of lime, and the greater part of the alcohol or ether distilled from the filtrate. The residue often yields crystals of the alkaloid in the course of a few days; in other cases, it is exactly neutralized with sulphuric or phosphoric acid, in order to obtain a crystallizable salt. With volatile,

alkaloids certain modifications of this process are required. (O. Henry, *J. Pharm.* 21, 222; abstr. *Ann. Pharm.* 15, 300.) The precipitate formed with the tannin may also be dissolved in alcohol; the tannin precipitated by sugar of lead; the excess of lead removed from the filtrate by sulphuretted hydrogen; and the alkaloid separated from the filtered solution of the acetate by an alkali, after sufficient concentration.

Further details will be given in treating of the individual alkaloids.

Preparation of Artificial Alkaloids.

1. By the dry distillation of azotized organic compounds.—Coal-tar contains Leucoline (Chinoline) and Crystalline (Aniline), which latter is produced more abundantly in the dry distillation of indigo. Tar from the dry distillation of bones contains Odorine, Olanine, Ammoline, and Animine (*vid.* p. 79).

2. By distilling azotized organic compounds with hydrate of potash. Quinine, Cinchonine, and Strychnine, thus treated, yield Leucoline (Chinoline).

3. By treating organic compounds containing nitrogen and sulphur with a fixed alkali, oxide of lead, or red oxide of mercury in the wet way. When Thiosinnamine, $C^8H^8N^2S^2$ ($=C^8H^4(CyS^2)Ad,H^2$), itself an alkaloid, is triturated with hydrated oxide of lead and water, 2 At. sulphide of lead are formed, 2 At. water separated, and another alkaloid, Sinnamine, $C^8H^6N^2$ ($=C^8H^4CyN,H^2$), is produced. 2 At. Oil of Mustard $=2(C^3H^5NS^2)=2(C^6H^5CyS^2)$, with 6 At. oxide of lead and 2 At. water, form 4 At. sulphide of lead, 2 At. carbonate of lead, and the alkaloid, Sinapoline, $C^{14}H^{13}N^2O^2$ ($=C^{12}H^8CyAdO^2,H^2$). Phenite of ammonia, kept in a sealed glass tube for some weeks at a temperature of 300°, yields a large quantity of Aniline:

$$C^{12}H^6O^2 + NH^3 = 2HO + C^{12}H^7N.$$

Furfurol, $C^{10}H^4O^2,O^2$, immersed in aqueous ammonia, is gradually converted into Furfuramide:

$$3(C^{10}H^4O^4) + 2NH^3 - 6HO = C^{30}H^{12}N^2O^6.$$

This furfuramide is not a base, but is immediately resolved by the action of dilute acids into ammonia and furfurol; but by boiling with dilute potash-ley, it is converted, without any evolution of ammonia, into the base, Furfurine, which is isomeric with it. The potash, therefore, alters the arrangement of the atoms. Furfuramide is probably $C^{30}H^{10}(NH^2)O^6$, and Furfurine, $C^{30}H^{10}N^2O^6,H^2$ (Nucleus = 30 : 18).

4. By treating certain nitro-compounds with hydrosulphuric acid or hydrosulphate of ammonia.—The process always consists in this: that 6HS are deprived of all their sulphur, which is precipitated, while 4H are transferred to the 4O of the NO^4 in the compound, whereby 4HO are separated, and in their stead 2H pass into the compound (p. 75). Thus, Nitrobenzide, $C^{12}H^5X$, is converted into Aniline, $C^{12}H^5N,H^2$; Nitrotoluide, $C^{14}H^7X$, into Toluidine, $C^{14}H^7N,H^2$; Nitronaphthaline, $C^{20}H^7X$, into Naphthalidam, $C^{20}H^7N,H^2$, &c.

5. By treating another alkaloid with oxide of manganese and sulphuric acid.—Thus, Narcotine yields Opianic acid and a new alkaloid, called Cotarnine.

¶ *Formation of the Compound Ammonias discovered by Wurtz and Hofmann.* (p. 16.)—*a.* By the action of caustic potash on the cyanates of methyl, ethyl, amyl, &c. (Wurtz), thus:

$$\underbrace{C^2H^3O,C^2NO}_{\text{Cyanate of methyl.}} + 2(KO,HO) = 2(KO,CO^2) + \underbrace{C^2H^5N}_{\text{Methylamine.}}$$

$$\underbrace{C^4H^5O,C^2NO}_{\text{Cyanate of ethyl.}} + 2(KO,HO) = 2(KO,CO^2) + \underbrace{C^4H^7N}_{\text{Ethylamine.}}$$

$$\underbrace{C^{10}H^{11}O,C^2NO}_{\text{Cyanate of amyl.}} + 2(KO,HO) = 2(KO,CO^2) + \underbrace{C^{10}H^{13}N}_{\text{Amylamine.}}$$

b. By the action of potash on acetyl-urea, $C^4H^6N^2O^2$, and metacetyl-urea, $C^6H^8N^2O^2$ (Wurtz):

$$C^4H^6N^2O^2 + 2(KO,HO) = 2(KO,CO^2) + H^3N + C^2H^5N;$$

$$C^6H^8N^2O^2 + 2(KO,HO) = 2(KO,CO^2) + H^3N + C^4H^7N.$$

c. By the action of the iodides and bromides of the alcohol-radicals on ammonia, aniline, and its derivatives, chloraniline, nitraniline, &c. (Hofmann.)

Bromide of ethyl with ammonia yields hydrobromate of *Ethylamine:*

$$H^3N + C^4H^5Br = C^4H^7N,HBr;$$

and by treating this salt with potash, the ethylamine may be set free in the form of a gas absorbable by water, just as ammonia is set free from hydrobromate of ammonia.—In a similar manner ethylamine acted upon by hydrobromic acid yields *Diethylamine,* $(C^4H^5)^2,H,N = C^8H^{11}N$; and this again acted upon by bromide of ethyl yields *Triethylamine,* $(C^4H^5)^3N = C^{12}H^{15}N$. This last compound does not appear to be acted upon by excess of bromide of ethyl, or at least to a very slight extent only; but the iodide of ethyl acts upon it with facility, forming an iodide of *Tetrethylium:*

$$C^{12}H^{15}N + C^4H^5I = (C^4H^5)^4NI.$$

And the solution of this salt, treated with oxide of silver, yields a precipitate of iodide of silver and a strongly alkaline solution containing the *hydrated oxide of tetrethylium,* $(C^4H^5)^4NO,HO$, which, by evaporation in vacuo in presence of sulphuric acid and lime, may be obtained in the solid state, forming in fact a fixed alkali, like hydrate of potash.

When iodide of methyl is treated with concentrated aqueous ammonia, five different iodides are formed, viz.: Iodide of ammonium, $H^4N.I$; iodide of *methylium,* $H^3,C^2H^3,N.I$; iodide of *dimethylium,* $H^2,(C^2H^3)^2,N.I$; iodide of *trimethylium,* $H,(C^2H^3)^3,N.I$; and iodide of *tetramethylium,* $(C^2H^3)^4,N.I$. The last, when separated by crystallization, redissolved, and treated with oxide of silver, yields a solution, from which, by evaporation, the hydrated oxide of tetramethylium may be obtained in the solid state, and exhibiting properties similar to those of the tetrethylium-compound.—Iodide of amyl treated with ammonia yields similar results, though not so readily.

The action of iodide of methyl on triethylamine yields the iodide of *methylotriethylium,* $(C^2H^3,C^4H^5),N.I$, from which a crystalline hydrated oxide may be obtained by the method above described.—Similar results by the action of iodide of amyl on triethylamine.

Iodide of methyl acting on diethylamylamine yields iodide of *methylodiethylamylium,* $\{C^2H^3,(C^4H^5)^2,C^{10}H^{11}\}N.I$.

Aniline, which may be regarded as *Phenylamine*, $H^3(C^{12}H^5)N$, yields, when treated with excess of bromide of ethyl, the hydrobromate of *Ethylaniline* or *Ethylophenylamine*, $H,(C^4H^5),(C^{12}H^5),N=C^{16}H^{11}N$; thus:

$$C^{12}H^7N + C^4H^5Br = C^{16}H^{11}N,HBr;$$

and this, when decomposed by caustic potash, yields the base in the form of an oily liquid resembling aniline, but differing from it by a slight difference of odour, a higher boiling point, and a lower specific gravity.—By precisely similar actions a great number of similar compounds may be formed; *e.g.*, Diethylaniline, $(C^4H^5)^2,(C^{12}H^5),N=C^{20}H^{15}N$; *Ethylochloraniline*$=H(C^4H^5)C^{12}\left.\begin{matrix}H^4\\Cl\end{matrix}\right\}N=C^{16}H^{10}ClN$, &c. ¶

Properties. All alkaloids, excepting coniine, picoline, and some of the compound ammonias, are heavier than water. [Sp. gr. of ethylamine=0·6964 at 8°; of amylamine, 0·7503 at 18° (Wurtz); of ethylaniline, 0·954 at 18°; of diethylaniline, 0·939 at 18°. (Hofmann.)] Those which contain comparatively small numbers of carbon-atoms, and nothing but hydrogen and nitrogen in addition, are watery or oily liquids; thus nicotine, coniine, aniline, leucoline, and picoline, are oily liquids; most of the compound-ammonias are watery liquids; but those derived from aniline are oily. The bases analogous to oxide of ammonium form solid hydrates.—Those alkaloids which contain oxygen are solid, and mostly crystalline, and fuse when strongly heated, generally without decomposition. Almost all the alkaloids are colourless, the only exceptions being seminaphthalidam, which is yellow, and harmaline, which is yellowish brown. The solutions of all the natural alkaloids examined by Bouchardat exhibit a rotatory action on polarized light; but, according to Laurent, this property is not possessed by those which are produced artificially. Thus, nicotine, $C^{10}H^5N,H^2$, turns the plane of polarization 93·5° to the left; but aniline, $C^{12}H^5N,H^2$, which closely resembles it in composition, appears indifferent to polarized light, as likewise do amarine and lophine.

Methylamine is gaseous at ordinary temperatures, and does not liquefy till cooled below 0°. (Wurtz.) The other alkaloids consisting wholly of carbon, hydrogen, and nitrogen, are liquid at ordinary temperatures, and their boiling points lie between 18° (ethylamine) and 300°; they may, for the most part, be distilled without decomposition out of contact of air, those only which have very high boiling points suffering decomposition when distilled. Alkaloids containing oxygen and sulphur, on the contrary, are wholly or for the most part decomposed by distillation.

¶ The bases analogous to oxide of ammonium are decomposed by heat in a very remarkable manner. A moderately concentrated solution of oxide of tetrethylium may be boiled without alteration; but as soon as the base becomes nearly dry, it is decomposed, even at the heat of the water-bath, yielding water, triethylamine, and olefiant gas.

$$(C^4H^5)^4NO = HO + (C^4H^5)^3N + C^4H^4.$$

Oxide of tetramylium is decomposed in a similar manner; but oxide of tetramethylium undergoes a different kind of decomposition, which has not yet been fully examined; it yields, however, like the other two bases, a volatile alkaline distillate. Oxide of amylotriethylium yields water, diethylamylamine, and olefiant gas:

$$(C^4H^5)^3(C^{10}H^{11})NO = HO + (C^4H^5)^2(C^{10}H^{11})N + C^4H^4.$$

These bases appear indeed to form a connecting link between the volatile and the non-volatile alkaloids; for many of the fixed native alkaloids yield volatile bases when subjected to the action of heat or of potash; *e.g.*, quinine, cinchonine, strychnine, and pelosine, yield leucoline among their products of decomposition; while piperine gives picoline (?), and morphine, caffeine, codeine, and narcotine, have actually been converted into alcohol-bases, the former yielding methylamine, the two latter propylamine, $(C^6H^7)H^2N$. (Hofmann.) It is true that the decompositions of these native alkaloids are much more complicated than those of the artificial ammonium-bases; still a certain analogy appears to exist between them, and may perhaps pave the way to the artificial production of the fixed native alkaloids. (Hofmann.) ¶

Most alkaloids turn reddened litmus blue and violets green; *e.g.*, nicotine and morphine; the compound ammonias likewise exhibit strong alkaline reactions; but the weaker bases, such as narcotine, are neutral to vegetable colours, and like the earths, exhibit their basic character only in their behaviour with acids.

Only the most volatile alkaloids have any perceptible odour at ordinary temperatures, and these have generally a penetrating odour; *e.g.*, nicotine, coniine.—¶ Methylamine, ethylamine, and amylamine, smell very much like ammonia; the latter also has an odour like that of the amyl-compounds. The odour of the higher bases of this group is less ammoniacal; some of those derived from aniline are aromatic; trimethylamine and triethylamine have a peculiar fishy odour. ¶—The taste of most alkaloids is bitter; among them in fact are some of the bitterest substances known—strychnine, for example. A few others taste sharp, as veratrine; or aromatic and burning, as aniline and leucoline.—The alkaloids, so far as they have been examined, are distinguished by strong medicinal action. Some of them, as quinine, act as pure bitters; others as narcotics; some of them as strychnine, being in fact the most violent narcotic poisons known; others, as veratrine, exert an acid action; others, as nicotine, both acrid and narcotic; and, finally, some of them, as picoline, appear to act more in the manner of volatile oils.

Decompositions. Most alkaloids which are liquid at ordinary temperatures turn brown and become resinous when exposed to the air, the change being apparently accompanied by formation of ammonia; the compound ammonias, however, do not exhibit this change, with the exception of some of those derived from aniline.—The more fixed alkaloids, when subjected to dry distillation, yield carbonate of ammonia together with other products.—Many alkaloids, when treated with strong nitric acid, chlorine, bromine, iodine, &c., exhibit peculiar colours, probably in most cases accompanied by decompositions.

[Further details respecting these decompositions will be given in treating of the individual alkaloids.]

Combinations. Some alkaloids, such as nicotine and picoline, and most of the compound ammonias, mix with water in all proportions; others dissolve in it but sparingly, many requiring several hundred or thousand parts. Alcohol dissolves the alkaloids much more freely; ether dissolves many of them readily, but several of those which contain oxygen, cinchonine, and morphine for example, are nearly insoluble in that liquid.

In their combinations with acids, the alkaloids are analogous to ammonia (II., 426); for their compounds with hydrochloric and other

hydrogen-acids appear anhydrous after drying; but for the production of their oxygen-salts 1 At. of water is required; and this water remains in combination after the salt has been completely dried between 120° and 140°, and cannot be expelled without decomposing the salt. (Regnault.)—Thus, dried hydrochlorate of morphine=$C^{36}H^{19}NO^6$,HCl; and sulphate of morphine dried at 130°=$C^{36}H^{19}NO^6$,HO,SO^3. Similarly, hydrochlorate of aniline in the dried state=$C^{12}H^7N$,HCl; the sulphate=$C^{12}H^7N$,HSO^4.—The salts formed by the combination of an organic acid with the alkaloids contain for each atom of the alkaloid, 1 At. of the acid dried *per se*, or 1 At. water and 1 At. of the hypothetically anhydrous acid.—Some bases, as quinine and cinchonine, are capable of forming bibasic salts, which have a very weak alkaline reaction.

Most salts of the alkaloids are crystalline, some pulverulent and gummy. In consequence of their greater solubility, they generally exhibit the taste of the alkaloids in a much higher degree than the alkaloids themselves. Many of these salts are neutral, but others have an acid reaction; inasmuch as 1 At. of a strong acid is not completely neutralised by 1 At. of a weak base.

The solutions of most salts of the alkaloids may be evaporated to dryness without decomposition; if, however, they contain a volatile acid, and the alkaloid is a weak base, part or the whole of the acid is given off; similarly, the salts which contain a volatile alkaloid, give off part of it when heated, and the more readily as the acid is weaker.

In the circuit of the voltaic battery, the aqueous solutions of the alkaloid-salts deposit their alkaloid at the negative pole.—If the solution be not too dilute, cinchonine, quinine, or morphine, when thus treated, is separated in the form of a scaly deposit on the negative pole, or as a white cloud. (Brande, *J. Roy. Inst.* 1, 250; also *Schw.* 62, 82; also *Pogg.* 22, 308.) When an electric current is passed through a cup containing water acidulated with sulphuric acid, in which also is placed a voltameter *a* (Plate IV., Fig. 29) to receive the hydrogen gas, then through a cup containing an acidulated aqueous solution of the sulphate of the alkaloid, in which is placed a voltameter *b* for receiving the hydrogen, and another voltameter *c* for the oxygen, the following phenomena are observed: From quinine there are evolved, for every 116 vol. hydrogen in *a*, not 58 but only 44 vol. oxygen gas in *c;* with strychnine, the proportion=59 : 24; with morphine=40 : 10; and with narcotine=60 : 24. Hence the quantity of oxygen gas evolved from the solution of the alkaloid is not so great as might be expected from the indications of the voltameter *a;* the oxygen gas evolved is likewise mixed with a large quantity of nitrogen; *e.g.*, in the case of quinine, from 23 to 31 per cent., and in that of strychnine, about 25 per cent. [Hence it would appear that part of the oxygen evolved at the positive pole oxidates the carbon or hydrogen of the alkaloid, and liberates nitrogen gas.]—But the hydrogen gas collected in the voltameter *b* from the solution of the alkaloid is pure; and its quantity approaches more nearly to that in the voltameter *a*, in proportion as the solution of the alkaloid has been acidulated with a larger quantity of sulphuric acid; in this case, the hydrogen gas in *a* is to the hydrogen gas in *b* as 70 : 68, with quinine, and 90 : 80 with narcotine. When a neutral solution of sulphate of strychnine is used, 4 cubic centimetres of hydrogen collect in the voltameter *a*, in the same time that 1·6 cub. cent. of pure oxygen collect in the voltameter *c*, and 0·027 grm. of strychnine are separated at the positive pole. Hence it appears that (contrary to what takes place with the salts of inorganic bases), the action of the electric current is divided, one portion

decomposing the water of the alkaloid solution into 1·6 oxygen gas and 3·2 cub. cent. hydrogen, while the other portion, which, according to the voltameter *a*, corresponds to 0·8 cub. cent. of hydrogen, decomposes the strychnine-salts, separating from it a quantity of strychnine equivalent to the 0·88 cub. cent. hydrogen. For 0·88 cub. cent. hydrogen weigh 0·00007208 grm.; and this multiplied by 350 (the approximate atomic weight of strychnine), yields 0·025228 grm., which accords pretty well with the quantity 0·027 grm. actually obtained. (Matteucci, *Ann. Chim. Phys.* 74, 105.) [The experiment admits, however, of another interpretation. A current which, in the voltameter *a*, sets free 4 cubic centimetres, or 0·0003604 grm. hydrogen, should separate 350 times this quantity, or 0·12614 grm. of strychnine; and that only 0·027 grm. is separated arises partly from some of the strychnine remaining dissolved in the liquid, and partly from a portion being decomposed by the oxygen at the positive pole, in consequence of which also the oxygen evolved is less than it should be, and not quite pure. (Gm.)]

From the aqueous solutions of their salts, the alkaloids are precipitated by all inorganic alkalis, by magnesia, and by a few of the stronger bases of the heavy metals, and according to their peculiar nature, sometimes in crystals, flakes, or gelatinous masses, sometimes in oily drops like aniline; sometimes again they remain dissolved in the watery liquid, and volatilize when heated, like nicotine and most of the compound ammonias. — An excess of the caustic alkalis re-dissolves certain alkaloids, *e.g.*, morphine and atropine.—Alkaline monocarbonates likewise precipitate the salts of the fixed alkaloids; bicarbonate of potash or soda generally precipitates them even in the cold, but more quickly on boiling; if, however, the solution contains tartaric acid, certain of the alkaloids, such as cinchonine and narcotine, are no longer precipitated at ordinary temperatures by alkaline bicarbonates.

Since the fixed alkaloids yield sparingly soluble salts with certain inorganic acids, the aqueous solutions of the more soluble alkaloids form precipitates with the above-mentioned acids, and especially with their neutral ammoniacal or potash salts, the precipitation being more rapid as the solution is stronger.

Phosphate of Soda, for example, precipitates the salts of quinine, bebeerine, morphine, narcotine, strychnine, brucine, solanine, veratrine, and delphinine, the precipitates being crystalline in some cases and flocculent in others.

Iodide of Potassium precipitates the salts of cinchonine, bebeerine, strychnine, brucine, morphine, codeine, narcotine, veratrine, delphinine, and emetine; sometimes in the crystalline, sometimes in the pulverulent or flocculent state.

Aqueous Biniodide of Potassium (III., 50), added to many alkaline salts, throws down crystalline compounds of a hydriodate of the alkaloid, with 1 or 2 At. iodine more (sometimes there is formed a pulverulent, flocculent, or mucous precipitate, consisting of a mixture of several definite compounds). The precipitate forms with zinc or iron a soluble crystallizable compound of iodide of zinc or iodide of iron with the hydriodate of the alkaloid. Aqueous potash poured on the precipitate forms iodide of potassium, and the oxygen of the potash partly converts the alkaloid into another compound. (Bouchardat, *Compt. rend.* 9, 475; also *J. pr. Chem.* 19, 247.)

To this is, perhaps, related the brown-red precipitate which *Iodine*

dissolved in alcohol forms with the salts of quinine, cinchonine, morphine, strychnine, atropine, veratrine, emetine, &c.

Tincture of *Bromine* also forms a yellow precipitate with the salts of quinine, strychnine, and veratrine.

Aqueous *Iodic acid* or aqueous *Terchloride of Iodine*, added drop by drop and in excess to an alkaloid-salt dissolved in water, or better in alcohol, precipitates an acid iodate of the alkaloid. The iodic acid must be dissolved in a sufficient quantity of water to prevent its precipitation by the alcohol of the alkaloid solution; in the case of chloride of iodine, which is less soluble, this condition is spontaneously fulfilled. In this manner, the salts of cinchonine and quinine give precipitates, when dissolved in some thousand parts of alcohol; those of the other fixed alkaloids are precipitated when the solutions are more concentrated, but the salts of morphine decompose iodic acid without separation of iodine. —The precipitated acid iodate of the alkaloid is colourless and non-crystalline; deflagrates strongly, and without leaving charcoal, when heated, after drying, to a temperature between 115° and 120°, and often likewise by trituration; when exposed to the air it slowly turns brown. —The neutral iodates of the alkaloids are crystalline, colourless, and much more soluble in water and alcohol than the acid iodates; when heated, they fuse partially, and, after a while, detonate slightly but suddenly, with evolution of iodine and formation of a bulky charcoal; they may be also made to detonate by percussion, but not so strongly as the acid iodates.—Aqueous sulphurous acid separates the iodine from them. (Serullas, *Ann. Chim. Phys.* 45, 68; also *Pogg*, 20, 315.—*Ann. Chim. Phys.* 45, 274: also *J. chim. méd.* 6, 513.)—Coniine dissolved in alcohol is also precipitated by iodic acid.

The salts of the alkaloids, and in some cases also the aqueous and alcoholic solutions of the pure alkaloids, form with several salts of the noble metals, sparingly soluble precipitates, which are sometimes compounds of the alkaloid with the metallic salt; sometimes of the salt of the alkaloid with the metallic salt.

Solution of Corrosive Sublimate added to the solutions of the alkaloids in hydrochloric or other acids, or in some cases merely in water, forms flocculent or curdy precipitates, which generally contain 1 At. alkaloid to 1, 2, 3, or 4 At. chloride of mercury; viz., with aniline, 3HgCl; with leucoline, 2HgCl; with sinnamine, 2HgCl; with thiosinnamine, 4HgCl; with sinapoline, picoline, and nicotine (1HgCl); also with naphthalidam, cinchonine, quinine, morphine, narcotine, brucine, strychnine, veratrine, delphinine, and emetine; with tetrethylium it forms a beautiful white crystalline precipitate composed of $(C^4H^5)^4NCl,5HgCl$. (Coniine, atropine, solanine, and codeine are not precipitated). Many of these precipitates fuse just above 100°, forming yellow masses; they dissolve but sparingly in water and alcohol.

With *Protiodide of Mercury* also, most or all alkaloids enter into combination; hence most of their salts, even very dilute, form with iodide of mercury and potassium, white or yellowish white, pulverulent, or flocculent precipitates, which appear yellow after drying, and fuse when heated, giving off vapours of iodine. The precipitate formed with tetrethylium corresponds in composition to the chlorine-compound. (Hofmann.) (*Comp.* Caillot, *Ann. Chim. Phys.* 42, 263; also *Schw.* 59, 105; also *N. Tr.* 21, 1, 246).

Nitrate of silver precipitates but few of the alkaloids. The preci-

pitate obtained with alcoholic solution of strychnine and nitrate of silver, consists of 1 At. stychnine, 1 At. oxide of silver, and 1 At. nitric acid; it may, therefore, be regarded as nitrate of strychnine, in which the HO, necessary to the constitution of the salt, is replaced by AgO, or H by Ag.—Methylamine, ethylamine, and amylamine, precipitate oxide of silver, and redissolve it in excess, like ammonia. (Wurtz.)

Aqueous *Terchloride of Gold* and its compound with chloride of sodium, form with salts of picoline, animine, olanine, nicotine, coniine, quinine, cinchonine, bebeerine, corydaline, atropine, morphine, delphinine, and emetine, yellow precipitates, inclining to brown, red, or green, very slightly soluble in water, easily soluble in alcohol, but insoluble in ether; they appear to be compounds of terchloride of gold with the alkaloid. The precipitate formed by morphine soon turns bluish and violet from reduction of gold. (*Comp.* Larocque & Thibierge, *J. chim. méd.* 18, 696.) Solution of ethyl-aniline yields with terchloride of gold a yellow oily precipitate, easily decomposed. Chloride of tetrethylium forms a lemon-yellow precipitate, whose formula is $(C^4H^5)^4NCl,AuCl^3$. (Hofmann.)

Aqueous Bichloride of Platinum precipitates the salts of nearly all alkaloids, but not those of solanine. The yellow precipitate, which is sometimes crystallo-granular, sometimes pulverulent, contains, so far as it has yet been examined, 1 At. of hydrochlorate of the alkaloid, and 1 At. $PtCl^2$; in the case of sinnamine only, the precipitate appears to have a different composition, supposing that alkaloid to contain 8C. Some of the compound ammonia-salts of bichloride of platinum, form large crystals of great beauty and regularity, *e. g.*, the triethylamine and tetrethylium salts. (Hofmann.)

Protochloride of Palladium and *Bichloride of Iridium* also precipitate the salts of certain alkaloids.

Many organic acids and their compounds with alkalis, also precipitate the salts of certain alkaloids.

Sulphocyanide of Potassium precipitates the salts of cinchonine, quinine, bebeerine, strychnine, brucine, morphine, codeine, narcotine, veratrine, delphinine, and emetine. Several of these precipitates are acicular, others curdy; they dissolve when the aqueous mixture is heated, and separate out again as it cools; hot alcohol forms with them a bitter solution, which reddens ferric salts. (*Comp.* Artus, *J. pr. Chem.* 8, 253; O. Henry, *J. Pharm.* 24, 194.)

Oxalic acid and oxalate of potash precipitate the salts of cinchonine, quinine, and strychnine.

Picric acid precipitates either the salts or the alcoholic solutions of many alkaloids, forming flocculent or pulverulent yellow precipitates.

Tannic acid (tannin of nut-galls), and also the infusion or tincture of galls (the latter, however, is less adapted to the purpose, because the alcohol which it contains exerts a solvent action on the precipitate), precipitate the salts of many alkaloids, and apparently of all, viz., those of aniline, nicotine, coniine, sinnamine, cinchonine, quinine, cinchovatine, corydaline, aconitine, atropine, morphine, codeine, narcotine, cotarnine, narceine, strychnine, brucine, solanine, caffeine, theobromine, chelidonine, sanguinarine, veratrine, delphinine, and emetine. As the precipitate is soluble in acids, an excess of acid in the salt prevents the precipitation. (Wackenroder, *N. Br. Arch.* 28, 54.)

Before precipitating the solution of the alkaloid-salt with tannic-acid, it is proper to add to it a drop or two of sulphuric acid. All these pre-

cipitates are white, curdy, and dry up to a white powder, which, when heated, fuses into a brown resinous mass, flexible immediately after cooling, but afterwards becoming brittle and friable. They contain, at least in the case of cinchonine, quinine, strychnine, and brucine, 2 At. tannic acid (supposed=$C^{18}H^{8}O^{12}$), to 1 At. of the alkaloid.—If the precipitate, at least with quinine and cinchonine, be enclosed while yet moist, in atmospheric oxygen, it becomes, for the most part, soluble in water in the course of a few weeks, doubtless by the conversion of the tannic acid into gallic acid; for the solution gives a blue colour with ferric salts. The precipitate is decomposed by many inorganic bases, which abstract the tannic acid and set the alkaloid free; ammonia, potash, and soda, however, generally dissolve the whole of it. If the precipitate be made into a paste with baryta, lime, or magnesia, and a small quantity of water, it becomes green or bluish from decomposition of the tannic acid, and after drying, the alkaloid may be extracted in its original state by boiling alcohol. The hydrated oxides of antimony, tin, lead, and iron, extract the tannic acid, and the alkaloid may then be dissolved out by alcohol. The salts of these four oxides act in a similar manner, forming a soluble salt of the alkaloid, but the free acid contained in them may hold a portion of the tannate in solution. Lastly, the tannic acid may also be withdrawn by glue and moist parchment; the latter, however, soon ceases to act. The precipitated tannates are nearly unsoluble in cold water, but dissolve sparingly in hot water, the solution becoming turbid as it cools, and a brown resinous film being formed upon it. They dissolve in some dilute acids; also in alcohol, and at a boiling heat in spirit of 28° Bm.; the solution reddens litmus strongly, tastes rather rough than bitter, and does not yield crystals on evaporation. (O. Henry, *J. Pharm.* 21, 212.)

Gallic acid does not precipitate the salts of the alkaloids.

The composition of most of the non-oxygenated alkaloids is such, that they may be regarded, either (*a*), as compounds of nuclei, in which 1 or 2H is replaced by 1 or 2N, with 2H, (Gm.); or (*b*), as nuclei, containing 1 Ad in place of 1H, (Laurent); or (*c*), as copulated compounds of ammonia with an organic compound not known in the separate state, to which view Berzelius gives the preference. The following tables exhibit these several modes of viewing the composition of the alkaloids:

	Empirical Formula.				*a*				*b*				*c*				Primary Nucleus.	
	C	H	N		C	H	N, H		C	H	Ad		C	H	Am			
Nicotine	10	7	1	=	10	5	1, 2	=	10	5	1	=	10	4	1		10	6
Aniline	12	7	1	=	12	5	1, 2	=	12	5	1	=	12	4	1		12	6
Leucoline	18	7	1	=	18	5	1, 2	=	18	5	1	=	18	4	1		18	6
Toluidine	14	9	1	=	14	7	1, 2	=	14	7	1	=	14	6	1		14	8
Coniine	16	17	1	=	16	15	1, 2	=	16	15	1	=	16	14	1		16	16
Naphthalidam	20	9	1	=	20	7	1, 2	=	20	7	1	=	20	6	1		20	8
Seminaphthalidam	10	5	1	=	10	3	1, 2	=	10	5	1	=	10	3	1		10	4(?)

A few of these alkaloids contain 2N; *e. g.*, amarine=$C^{42}H^{18}N^{2}$, and lophine=$C^{46}H^{16}N^{2}$; and 1 At. of them, although it contains 2N, saturates but 1 At. acid. Amarine is derived from the nucleus $C^{14}H^{6}$, which taken three times gives $C^{42}H^{18}$; according to (*a*), we obtain the perfectly analogous formula, $C^{42}H^{16}N^{2},H^{2}$; but (*b*) gives $C^{42}H^{14}Ad^{2}$, so that there is a deficiency of 2H in the nucleus; according to (*c*) the formula is $C^{42}H^{12}Am^{2}$.—Sinnamine, $C^{9}H^{8}N^{2}$, may be regarded, according to (*a*), as

C^6H^4CyN,H^2 (nucleus=6 : 6); Thiosinnamine, $C^8H^6N^2S^2$, as C^6H^4 (CyS^2) Ad,H^2 (nucleus=6 : 6); and Sinapoline, $C^{14}H^{12}N^2O^2$ as $C^{12}H^8CyAdO^2,H^2$ (nucleus=12 : 12); the formulæ of the last two alkaloids, however, are so far doubtful, that the nitrogen in their nuclei exists, not as such, but in the form of cyanogen and amidogen. Melamine, $C^6H^6N^6$, is probably $C^6Ad^3N^4,H^2$ (nucleus=6 : 6).

¶ The alkaloids in the preceding table may, of course, be represented in a form similar to those already given for the bases discovered by Wurtz and Hofmann, *e. g.*,

$$\text{Nicotine} = \left.\begin{matrix} H \\ H \\ C^{10}H^5 \end{matrix}\right\}N; \quad \text{Toluidine} = \left.\begin{matrix} H \\ H \\ C^{14}H^7 \end{matrix}\right\}N, \text{ \&c.}$$

On the other hand, the compound-ammonias containing the alcohol-radicals, may be exhibited in the form *c;* thus Methylamine=(C^2H^3), NH^3; Ethylamine=(C^4H^4),NH^3; Dimethylamine=$(C^2H^3)^2$,NH^3; Methylethylamine=$(C^2H^3)(C^4H^4)$,NH^3; Triamylamine=$(C^{10}H^{10})^3$,NH^3; Tetrethylium=$(C^4H^5)^4$,NH^4. The forms *a* and *b* cannot well be adapted to these bases, inasmuch as they would make no distinction between those which are isomeric with each other, such as ethylamine and dimethylamine, methylethylamine and propylamine, which are quite distinct from one another in origin and properties, and give different products of decomposition. Similar isomeric relations exist also between some of these bases and other alkaloids, previously known and obtained from totally different sources; thus methylaniline is isomeric with toluidine, and methylethylaniline with cumidine; but these isomeric substances exhibit the most striking dissimilarity in their characters. This may, perhaps, be taken as a proof that the forms *a* and *b* are not true representatives of any of the alkaloids, as there can be little doubt that all these bodies are similarly constituted. ¶

Considering the uncertainty which still exists respecting the constitution of most of the oxygenated alkaloids, it may suffice to exhibit the composition of a few of those which are best known, as in the following table:

	Empirical formula.					According to *a*.					Nucleus.
	C	H	N	O		C	H	N	O, H		
Caffeine	16	10	4	4	.....	16	8	4	4, 2	.....	16 : 16
Furfurine	30	12	2	6	.....	30	10	2	6, 2	.....	30 : 18
Cinchonine	20	12	1	1	.....	20	10	1	1, 2	.....	20 : 12
Quinine	20	11	1	2	.....	20	9	1	2, 2	.....	20 : 12
Morphine	36	19	1	6	.....	36	17	1	6, 2	.....	36 : 24
Codeine	36	20	1	5	.....	36	18	1	5, 2	.....	36 : 24
Narcotine	46	25	1	14	.....	46	23	1	14, 2	.....	46 : 38
Cotarnine	26	13	1	6	.....	26	11	1	6, 2	.....	26 : 18
Strychnine	44	22	2	4	.....	44	20	2	4, 2	.....	44 : 26(?)
Brucine	48	26	2	8	.....	48	24	2	8, 2	.....	48 : 34(?)

We must not omit to notice, that for urea, $C^2H^4N^2O^2$, supposing it to belong to the organic alkaloids, the theory (*a*) cannot be satisfactorily carried out; in the formula C^2Ad^2,O^2, we find 20 outside the nucleus instead of 2H; the formula, C^2NAdO^2,H^2, requires a nucleus=2 : 4, and $C^2H^2N^2O^2,H^2$, a nucleus=2 : 6, whose existence is very doubtful. But urea is also distinguished from the true alkaloids by many other properties.

Berzelius (*J. pr. Chem.* 23, 231; *Lehrb.* 6, 269), regards the alkaloids as copulated compounds of ammonia with an organic compound, in which the ammonia retains its basic properties. If 1 At. of an alkaloid contains

more than 1 At. nitrogen, the excess belongs to the organic compound. This view is supported by the similarity of the ammoniacal and alkaloidal salts, with regard to the water which they contain, and by the fact that most alkaloids contain only 1 At. nitrogen. On the other hand, it is remarkable that the alkaloids, although, like other azotized substances, they give off ammonia when subjected to dry distillation, yet exhibit no signs of containing that substance ready formed. They do not give off ammonia when boiled with aqueous potash, and in many cases not even when fused with hydrate of potash; neither is ammonia extracted from them by dilute acids acting in excess and with the aid of heat. When chlorine-water is added to a saturated aqueous solution of coniine, not a trace of nitrogen is evolved even on heating the liquid; but if a few drops of ammonia be added, nitrogen is immediately given off. (O. Henry.) When strychnine, brucine, and other natural alkaloids, are decomposed by nitric acid, no nitrate of ammonia is found in the residue. (Liebig, *Pogg.* 21, 27.) When cyanate of silver is decomposed by nitrate of quinine, strychnine, morphine, atropine, &c., the liquid containing the cyanate of the alkaloid yields no urea when filtered from the chloride of silver and evaporated, but gives off carbonate of ammonia from decomposition of the cyanic acid, and leaves the alkaloid behind. (Liebig, *Ann. Pharm.* 6, 73.) We must, however, agree with Berzelius in not attaching any great importance to the last-mentioned experiment, inasmuch as the ammonia may be too intimately united with its copula, to be converted into urea in conjunction with the cyanic acid.

These circumstances, which render improbable the existence of ready-formed ammonia in the alkaloids, are likewise unfavourable to Laurent's supposition (*Compt. mensuels*, 1, 41), that they contain amidogen, inasmuch as the true amides, when treated with potash or with acids, yield ammonia with decomposition of water; it is, in fact, precisely by this circumstance, that furfuramide, which is not a base, is distinguished from furfurine, which is isomeric with it.

[For a particular view of the constitution of the alkaloids, *vid.* Couerbe, *Ann. Chim. Phys.* 56, 185.]

¶ The antimony-bases, viz., Stibmethyl, $(C^2H^3)^3$,Sb, Stibethyl, $(C^4H^5)^3$,Sb, and Stibamyl $(C^{10}H^{11})^3$,Sb, and the compounds Stibmethylium $(C^2H^3)^4$,Sb and Stibethylium $(C^4H^5)^4$,Sb, may also be regarded as alkaloids and metalloids belonging to the types of ammonia and ammonium, and corresponding respectively to triethylamine, tetrethylium, &c. — The compounds containing 3 atoms of the alcohol-radicals are obtained by distilling the iodides of methyl, &c., with antimonide of potassium. They are volatile liquids, having remarkably strong combining tendencies, uniting at ordinary temperatures with oxygen, sulphur, selenium, chlorine, iodine, &c, the act of combination being attended with considerable evolution of heat, sufficient in some cases to produce vivid combustion; thus, stibmethyl and stibethyl take fire by mere contact with the air.—The compounds containing 4 At. of the radicals have not yet been obtained in the separate state, but their iodides and bromides are obtained by the action of iodide or bromide of methyl or ethyl on stibmethyl or stibethyl, just as tetrethylium is formed by the action of iodide of ethyl on triethylamine. Of these compounds, stibmethylium is the one which has hitherto been most minutely examined. It forms a hydrated oxide, $(C^2H^3)^4NO+HO$, which, like the hydrated oxide of tetrethylium, is a white crystalline mass, having a highly caustic, alkaline taste, and analogous in all its relations to caustic potash, expelling

ammonia, and even baryta and lime, as well as all the heavy metallic oxides, from their combinations. Its chloride, iodide, bromide, sulphate, nitrate, &c., are precisely analogous to the corresponding ammonium-compounds.—An iodide of Stibmethylethylium, $(C^2H^3)^3(C^4H^5)Sb,I$, has likewise been obtained by treating stibmethyl with iodide of ethyl.—Bismethyl, $(C^4H^5)^3Bi$, obtained by treating iodide of ethyl with bismuth-potassium, is another base belonging to the ammonia-type, and possessing similar characters to stibethyl.—The phosphorus base, $(C^2H^3)^3P$, likewise belong to the same type. ¶

b. Compounds of Nuclei with Hydrogen and Oxygen in equal numbers of atoms.

a. Compounds of Nuclei with 1 *At. Hydrogen and* 1 *At. Oxygen.*

Ethers.

The few compounds of this order at present known to exist, are produced by heating the alcohols with substances which have a strong attraction for water, especially with oil of vitriol. These substances withdraw hydrogen and oxygen from the alcohol, and the ether distils over.—Thus, wood-spirit or methylic alcohol, C^2H^4,H^2O^2, yields methylic ether, C^2H^3,HO, and common alcohol, C^4H^6,H^2O^2, yields common ether, C^4H^5,HO. Amylic ether, $C^{10}H^{11},HO$, is produced in the decomposition of chloride of amyl by potash:

$$C^{10}H^{10},HCl + KO = C^{10}H^{10},HO + KCl.$$

These compounds may also be expressed by the formulæ: C^2HO,H^2, —C^4H^3O,H^2,—and $C^{10}H^9,H^2$, a mode of viewing their composition which is recommended by many of their reactions.

In the radical theory, the ethers are regarded as C^2H^3,O,—C^4H^5,O,—$C^{10}H^{11},O$, &c., that is to say, as oxides of the metalloidal radicals, methyl, C^2H^3, ethyl, C^4HC^5, and amyl, $C^{10}H^{11}$.

Gerhardt and others double the atomic weights of these compounds, writing, for example, the formula of common ether, $C^8H^{10}O^2$, so as to get rid of uneven numbers of atoms and obtain a diatomic gas; for C^4H^5O would give a monatomic gas (p. 54). This view, however, does not accord with the low boiling points of the ethers, or with the circumstance that common ether, for example (unless it be subjected to a red heat), does not yield any product of decomposition containing more than 4 At. carbon.

	Empirical Formula.	*Th.* 1,	*Th.* 2,	or:
Methylic ether	C^2H^3O	$=C^2H^2,HO$	$=C^2HO,H^2$	
Chlorinated	C^2H^2ClO	$=C^2HCl,HO$	$=C^2HO,HCl$	$=C^2ClO,H^2$
	C^2HCl^2O	$=C^2Cl^2,HO$	$=C^2ClO,HCl$	
	C^2Cl^3O	$=C^2Cl^2,ClO$	$=C^2ClO,Cl^2$	
Common or Vinic Ether	C^4H^5O	$=C^4H^4,HO$	$=C^4H^3O,H^2$	
With chlorine	C^4H^4ClO	$=C^4H^3Cl,HO$	$=C^4H^3O,HCl$	$=C^4H^2ClO,H^2$
	$C^4H^3Cl^2O$	$=C^4H^2Cl^2,HO$	$=C^4H^2ClO,HCl$	$=C^4HCl^2O,H^2$
	C^4Cl^5O	$=C^4H^4ClO$	$=C^4Cl^3O,Cl^2$	
With chlorine and sulphur	C^4H^3ClSO	$=C^4H^2ClS,HO$	$=C^4HClSO,H^2$	
With sulphur	$C^4H^3S^2O$	$=C^4H^2S^2,HO$	$=C^4HS^2O,H^2$	
Amylic ether	$C^{10}H^{11}O$	$=C^{10}H^{10},HO$	$=C^{10}H^9O,H^2$	

The term *Ether*, or more rarely, *Naphtha*, had been long used to denote certain compounds distinguished by their volatility, odour, taste, slight solubility in water, &c., and obtained by treating alcohol with various acids, metallic chlorides, &c. Afterwards, when wood-spirit and fusel-oil were discovered, the term ether was extended to the corresponding compounds obtained by similar methods from these alcohols. It has since, however, been found that the products thus included under the term ether must be divided, according to their composition, into three classes:

1. Some may be regarded as Alcohol—1HO, or as Nucleus + HO. The French chemists designate them as *Ethers of the first class* (*Ethers du première genre*). These compounds are best denoted by the old term *Ether*. Thus C^2H^3O=methylic or formic ether (*Holzäther* oder *Formäther*); C^4H^5O=vinic or common ether (*Vinäther*); $C^{10}H^{11}O$=amylic ether (*Mylather*).

2. Other compounds belonging to the same type, and generally obtained by treating an alcohol with a hydrogen-acid, may be regarded as ethers of the first class, in which the 1 At. oxygen is replaced by 1 At. of the radical of a hydrogen-acid. To this class belong, for example, C^4H^5S,—C^4H^5I,—C^4H^5Cl, &c.: *Ethers du deuxième genre.* The vapour of the corresponding sulphur-compounds is monatomic, like that of the ethers of the first class; but that of all other ethers of the second class is diatomic. I formerly denoted these compounds by the term: *Naphthas produced by hydrogen-acids* (*Naphthen durch Wasserstoffsäuren erzeugt*), but I now propose for them the term *Afer*, which recalls the sound of the words Ether and Naphtha: *e. g.*, *Formafer*, *Vinafer*, and *Mylafer*. To these names are prefixed those of the acid radical; thus, *Chlor*-Vinafer= C^4H^5Cl.

3. Lastly, many etheriform compounds produced from alcohols by oxygen-acids may be regarded as compounds of an ether of the first class with an oxygen-acid, organic or inorganic, the former being supposed to be in the hypothetically anhydrous state: *Ethers du troisième genre.* I formerly distinguished these compounds by the name of *Naphthas produced by oxygen-acids* (*Naphthen durch Sauersoffsäuren erzeugt*); but I now propose for them the term *Ester*. Thus, C^2H^3O = *Schwefel-Formester*; C^4H^5ON,O^3 = *Salpetrig-Vinester*; and $C^{10}H^{11}O,C^2HO^3$ = *Ameisen-Formester*.*

* It is scarcely necessary to observe that the nomenclature of the ethers explained in the last two paragraphs is specially adapted to the German language. It would not perhaps be difficult to devise corresponding terms in English; but it will be better, in the translation, to adopt the terms commonly used in English works, such terms being perfectly definite and intelligible: thus, for ethers of the first class, we have C^2H^3O = *methylic ether* or *methyl-ether*; C^4H^5O = *common ether*, *vinic ether*, or *ethyl-ether*; $C^{10}H^{11}O$ = *amylic ether* or *amyl-ether*.—For ethers of the second class: C^4H^5Cl = *chloride of ethyl*, *ethylic chloride*, or *hydrochloric ether*; C^2H^3I = *iodide of methyl*, *methylic iodide*, or *hydriodic methyl-ether*; $C^{10}H^{11}Br$ = *bromide of amyl*, *amylic bromide*, or *hydrobromic amyl-ether*, &c.—For the ethers of the third class, a precisely similar nomenclature may be used, viz., C^4H^5O,NO^3 or C^4H^5,NO^4 = *nitrite of ethyl*, *ethylic nitrite*, or *nitrous ether*; C^2H^3O,SO^3 or C^2H^3,SO^4 = *sulphate of methyl*, *methylic sulphate*, or *sulphuric methyl-ether*; $C^{10}H^{11}O,C^2HO^3 = C^{10}H^{11},C^2HO^4$ = *formiate of amyl*, *amylic formiate*, or *formic amyl-ether*. It is true that these terms are more especially adapted to the radical theory, which the author rejects; but as this theory is universally adopted in England, and is rapidly gaining ground even among those continental chemists who have hitherto been its chief opponents, there is no necessity for departing from the nomenclature generally used. [W.]

¶ A fourth class is formed by the compound ethers discovered by Williamson (p. 17), the names and formulæ of which, as given by himself, are as follows:

(1) Three-carbon ether, Methylate of Ethyl, *or* Ethylate of Methyl ..... $\left.\begin{matrix}CH^3\\C^2H^5\end{matrix}\right\}O = C^3H^8O$

(2) Six-carbon ether, Methylate of Amyl, *or* Amylate of Methyl ..... $\left.\begin{matrix}CH^3\\C^5H^{11}\end{matrix}\right\}O = C^6H^{14}O$

(3) Seven-carbon ether, Ethylate of Amyl, *or* Amylate of Ethyl ..... $\left.\begin{matrix}C^2H^5\\C^5H^{11}\end{matrix}\right\}O = C^7H^{16}O$

According to the atomic weights adopted in this Hand-book, these compound ethers must be regarded as formed from 2 At. of water, H^2O^2, the 2H being replaced by different radicals: thus—

(1) Methylate of Ethyl $= \left.\begin{matrix}C^2H^3\\C^4H^5\end{matrix}\right\}O^2 = C^6H^8O^2$

(2) Methylate of Amyl $= \left.\begin{matrix}C^2H^3\\C^{10}H^{11}\end{matrix}\right\}O^2 = C^{12}H^{14}O^2$

(3) Ethylate of Amyl $= \left.\begin{matrix}C^4H^5\\C^{10}H^{11}\end{matrix}\right\}O^2 = C^{14}H^{16}O^2$

The formulæ $C^6H^8O^2$, &c., assimilate these compounds to the alcohols, and in that light they have indeed been regarded by some chemists. (*Vid. Gregory's Handbook of Organic Chemistry*, 3rd edit. p. 252.) According to Williamson's notation, however, they really belong to the first class of ethers, common ether being in fact $\left.\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right\}O$, or $\left.\begin{matrix}C^4H^5\\C^4H^5\end{matrix}\right\}O^2$. ¶

β. Compounds of Nuclei with 2 At. Hydrogen and 1 At. Oxygen.

Alcohols.

The true alcohols at present known to exist are as follows:

	Crude Formula.				*Theory* 1.				*Theory* 2.				
	C	H	O		C	H, H	O		C	H	O, H	O	
Wood-spirit	2	4	2	.....	2	2	2	.....	2	1	1	3	1
Common Alcohol	4	6	2	.....	2	4	2	.....	4	3	1	3	1
Butylic Alcohol	8	10	2	.....	8	8	2	.....	8	7	1	3	1
Amylic Alcohol.....	10	12	2	.....	10	10	2	.....	10	9	1	3	1
Caprylic Alcohol	16	18	2	.....	16	16	2	.....	16	15	1	3	1
Ethal.....	32	34	2	.....	32	32	2	.....	32	31	1	3	1
Cerotin	54	56	2	.....	54	54	2	.....	54	53	1	3	1
Melissin.....	60	62	2	.....	60	60	2	.....	60	61	1	3	1

Wood-spirit is produced by dry distillation; common alcohol, and apparently also butylic and amylic acid, by fermentation; ethal, by treating spermaceti with potash; caprylic alcohol from castor-oil; cerotin from Chinese-wax; and melissin from bees-wax.

Even if the first theory be adopted, it is not necessary to suppose that the alcohols are compounds of a nucleus with 2 At. water, but that the 2 At. hydrogen and 2 At. oxygen attach themselves *separately* to different parts of the nucleus, without uniting together in the form of water. It is only when substances having a great affinity for water, such as sulphuric acid, phosphoric acid, &c., act upon the alcohols, that the hydrogen and oxygen are disposed to unite and form water. Under these circumstances, sometimes 1 At. oxygen and hydrogen are removed, and there remains an ether,—sometimes 2 At. and the nucleus is left in the free state.

According to the radical theory, the alcohols are hydrates of the compounds of methyl, ethyl, amyl, &c., with 1 At. O. Thus, Wood-spirit = hydrated oxide of methyl = C^2H^3O,HO; Alcohol = hydrated oxide of ethyl = C^4H^5O,HO; and Fusel-oil = hydrated oxide of amyl = $C^{10}H^{11}O,HO$. But ether dissolved in water does not form alcohol.—¶ Williamson regards the alcohols as formed from water, $\overset{H}{H}O$, by the substitution of 1 At. methyl, ethyl, &c., for 1 At. H; thus, wood-spirit = $\overset{CH^3}{H}O$; alcohol = $\overset{C^2H^5}{H}O$; fusel-oil = $\overset{C^5H^{11}}{H}O$. ¶

By the comparatively feeble action of oxygen in various ways, many of the alcohols are deprived of 2 At. hydrogen and converted into aldides, *e. g.*, common alcohol into common aldehyde, C^4H^4,O^2. In other cases, 2 At. oxygen likewise unite with the nucleus, and a monobasic acid is produced.—In this manner, wood-spirit may be converted into formic acid, C^2H^2,O^4; alcohol into acetic acid, C^4H^4,O^4; fusel-oil into valerianic acid, $C^{10}H^{10},O^4$; and ethal into ethalic acid, $C^{32}H^{32},O^4$. Hydrate of potash acting upon the alcohols at high temperatures, also converts them, with evolution of hydrogen, into the same acids (p. 134).

The alcohols form with many hydrogen-acids—the action being attended with separation of 2 At. water—a series of ethereal compounds (ethers of the second class), which may be regarded as ethers in which 1 At. oxygen is replaced by 1 At. of the radical of the hydrogen-acid. With oxygen-acids they form, either a similar series of ethereal compounds (ethers of the third class), or, with a double proportion of acid, a series of copulated acids.

Doubtful Alcohols.

	C H Cl O	C H Cl O,H O	C H Cl O, H O
Acetone	6 6 2 =	6 4 2 2 =	6 3 1 3 1
Mesitic Choral	6 4 2 2 =	6 2 2 2 2 =	6 3 2 1 3 1
Hydrochinone	12 6 4 =	12 4 2 2 2 =	12 3 3 3 1
Chlorhydrochinone	12 5 1 4 =	13 3 1 2 2 =	12 2 1 3 3 1
Saligenin	14 8 4 =	14 6 2 2 2 =	14 5 3 3 1
Chlorosaligenin	14 7 1 4 =	14 5 1 2 2 =	14 4 1 3 3 1

With regard to acetone and mesitic chloral, it is very doubtful whether they belong to this type (*vid. Ketones*); the rest of the above-named compounds deserve more particular examination with respect to their alcoholic character.—The following compounds may perhaps also be classed in the same category: Turpentine-camphor, $C^{20}H^{20}O^4 = C^{20}H^{16},H^4O^4$; Milk-sugar, $C^{24}H^{20}O^{20} = C^{24}H^{18}O^{18},H^2O^2$; common sugar, $C^{24}H^{22}O^{22} = C^{24}H^{18}O^{18},H^4O^4$; and grape-sugar, $C^{24}H^{24}O^{24} = C^{24}H^{18}O^{18},H^6O^6$.

c. Compounds of the Nuclei with Oxygen.

a. Compounds with 2 At. Oxygen.

Aldehydes in general, or Aldides.

When Liebig, by withdrawing 2 At. hydrogen from alcohol, converted it into the compound $C^4H^4O^2$, he called that compound *Aldehyde*, from

*Al*cohol and *dehyd*rogenation. More recently, a considerable number of other compounds have been discovered, possessing a certain analogy with Liebig's aldehyde, and to these the same name has been extended. To avoid this confusion, I propose to denote all these compounds by the generic term *Aldide*, reserving the original title of Aldehyde for the aldide of the ethyl-series.

The aldides are divided into the following classes, according to the nature of the nuclei in which 2 At. of oxygen are replaced;—we shall give a few examples of each class.

1. *Aldides of Primary Nuclei.*

C	H, O		C	H, O	
4	4, 2	Aldehyde.	14	8, 2	Anisol.
6	4, 2	Acrolein.	14	12, 2	Cuminol.
8	8, 2	Butyric Aldide.	14	14, 2	Œnanthol.
10	10, 2	Valeric Aldide.	18	8, 2	Oil of cinnamon.
12	6, 2	Phenous acid.	20	18, 2	Borneo-camphor.
12	10, 2	Mesitic ether (?).	32	32, 2	Spermaceti.
14	6, 2	Oil of Bitter Almonds.			

Most of these aldides have a tendency to take up two additional atoms of oxygen from the air, from oxide of silver, from nitric acid, &c., and to be thereby converted into monobasic acids. In this manner, aldehyde is converted into acetic acid; acrolein into acrylic acid; butyric aldide into butyric acid; bitter almond oil into benzoic acid; cuminol into cuminic acid; œnanthol into œnanthylic acid; and oil of cinnamon into cinnamic acid. This tendency is likewise exhibited in certain aldides of the chlorine-nuclei, whereby acids are formed containing chlorine-nuclei.

2. *Aldides of Oxygen-nuclei.*

a. Most of these compounds are produced by heating an acid either by itself or with anhydrous phosphoric acid. By this process the monobasic acids are reduced, with loss of 1 At. water, and the bibasic acids with the loss of 2 At. water, to the hypothetically anhydrous state, in which, according to the radical theory, they exist, together with a metallic oxide, in their metallic salts when dried as much as possible. In this state, however, they are no longer acids (pp. 13, 14), but must be regarded, according to Laurent, as *Anhydrides*. In contact with water or with aqueous alkalis, however, they recover the hydrogen and oxygen which they have lost, and are reconverted into the acids from which they originated. It is remarkable that, with the exception of maleic acid, none of those acids whose nuclei consist only of carbon and hydrogen, are capable of being reduced to this state. (*Vid.* p. 201.)

We must suppose that, in the conversion of an acid into an anhydride, the hydrogen withdrawn from the nucleus is replaced by oxygen outside the nucleus; but when water acts upon the anhydride, this oxygen is again removed from the nucleus, to give place to the hydrogen of the water. The explanation becomes simpler if we suppose, according to *Theory* 2 (p. 147), that the portion of hydrogen in an acid which can be replaced by a metal, viz., 1H in a monobasic, and 2H in a bibasic acid, is situated outside the nucleus, and these 1 or 2 At. H thus externally attached are given off in the formation of the anhydride, together with 1 or 2 At. O of the envelope.

Some of these anhydrides, that of camphoric acid, for example,

although they have no acid reaction, yet unite with bases, and form saline compounds, which, however, are quite distinct from those which are formed by the true acids.

In contact with water, the anhydrides are reconverted more or less quickly, into the original acids, the change being accelerated by the aid of heat or by the presence of an alkali. But camphoric anhydride remains unchanged, even after two hours' boiling with water; whereas the stronger acids separate it from its peculiar combinations with potash, oxide of lead, &c., in the form of ordinary camphoric acid. In some few cases, the anhydride is converted by the action of water, not into the original acid, but into another acid isomeric with it; thus, the anhydride into which itaconic acid is converted by heat, is slowly transformed by the action of water into citraconic acid, which is isomeric with itaconic acid.

If these anhydrides are to be regarded as dehydrated acids, we must also, as Gerhardt observes, consider common camphor, $C^{20}H^{16}O^2$, as a dehydrated acid; since, when heated with water, it takes up H^2O^2, and is converted into camphoric acid, $C^{20}H^{18}O^4$.

[For Gerhardt's researches on the anhydrides of organic acids, *vid.* p. 201.]

The following Acids yield the following Anhydrides:

	C	H	O, O	− HO =	C	H	O, O	
Maleic acid	4	2	4	1	4	1	1, 2	Maleic anhydride.
Lactic acid	6	6	2, 4	1	6	5	3, 2	Lactic anhydride.
Succinic acid	8	6	2, 6	2	8	4	4, 2	Succinic anhydride.
Tartaric acid	8	6	6, 6	2	8	4	8, 2	Tartaric anhydride.
Itaconic acid	10	6	2, 6	2	10	4	4, 2	Itaconic anhydride.
Phthalic acid	16	6	2, 6	2	16	4	4, 2	Phthalic anhydride.
Camphoric acid	20	16	2, 6	2	20	14	4, 2	Camphoric anhydride.

Chlorophthalic and nitrophthalic anhydrides, which will be mentioned hereafter, also belong to this head.

b. The following aldides of oxygen-nuclei are not produced by dehydrating the acids; but one at least among them, viz., benzil, when boiled with aqueous potash, takes up H^2O^2, and is converted into an acid, viz., benzilic acid; and hydranisyl, which is insoluble in aqueous potash, disappears when boiled for a long time with it, probably from a similar cause. Hydranisyl resembles the aldides of the primary nuclei in this respect, that when exposed to the air, it is gradually converted into anisic acid, $C^{20}H^{12}O^2,O^4$. Similarly, salicylous acid is converted by various oxidizing agents, into salicylic acid, $C^{14}H^6O^6$.

$C^{12}H^4O^2,O^2$	Chinone.	$C^{20}H^{12}O^4,O^2$	Parsley-camphor (?).
$C^{14}H^6O^2,O^2$	Salicylous acid.	$C^{20}H^{12}O^2,O^2$	Caryophyllic acid (?).
$C^{16}H^8O^2,O^2$	Hydranisyl.	$C^{28}H^{10}O^2,O^2$	Benzil.
$C^{18}H^6O^2,O^2$	Cumarine.	$C^{48}H^{30}O^2,O^2$	Pinic acid (?).

3. *Aldides of Iodine, Bromine, and Chlorine-nuclei.*

C^4HI^3,O^2	Iodal.	$C^{14}H^5I,O^2$	Iodobenzoyl.
C^4HBr^3,O^2	Bromal.	$C^{14}H^5Br,O^2$	Bromobenzoyl.
C^4HCl^3,O^2	Chloral.	$C^{14}H^5Cl,O^2$	Chlorobenzoyl.
C^4Cl^4,O^2	Chloraldehyde.	$C^{14}H^7Br,O^2$	Bromanisol.
C^8H^7Cl,O^2	Chlorabutyraldide.	$C^{14}H^7Cl,O^2$	Chloranisol.
$C^8H^6Cl^2,O^2$	Chlorebutyraldide.	$C^{16}H^4BrNO^2,O^2$	Bromisatine.
$C^8H^4Cl^4,O^2$	Chlorobutyraldide.	$C^{16}H^3Br^2NO^2,O^2$	Bibromisatine.
$C^{12}H^3Br^3,O^2$	Bromophenissic acid.	$C^{16}H^4ClNO^2,O^2$	Chlorisatine.
$C^{12}H^4Cl^2,O^2$	Chlorophenessic acid.	$C^{16}H^3Cl^2NO^2,O^2$	Bichlorisatine.
$C^{12}H^3Cl^3,O^2$	Chlorophenissic acid.	$C^{18}H^4Cl^4,O^2$	Chlorocinnose.
$C^{12}HCl^5,O^2$	Chlorophenussic acid.		

The following contain oxygen also in the nucleus:

$C^{12}HCl^3O^2,O^2$	Chlorochinone.	$C^{14}H^5BrO^2,O^2$	Bromosalicylous acid.
$C^{12}Cl^4O^2,O^2$	Chloranil.	$C^{16}H^4Cl^2O^2,O^2$	Chlorophthalic anhydride.
$C^{14}H^5ClO^2,O^2$	Chlorosalicylous acid.		

4. *Aldides of Azo-nuclei.*

C^2HN,O^2	Cyanic acid.	$C^{28}H^{11}N,O^2$	Benzilimide (?)
$C^{16}H^5NO^2,O^2$	Isatine.	$C^{42}H^{15}NO^2,O^2$	Picryl (?)
$C^{16}H^6NO,O^2$	Isatane.		

5. *Aldides of Amidogen-nuclei.*

C	H	N	O		
2	4	2	2	$= C^2Ad^2,O^2$	Urea.
4	4	2	4	$= C^4Ad^2O^2,O^2$	Oxamide.
6	7	1	4	$= C^6H^5AdO^2,O^2$	Lactamide.
8	6	2	4	$= C^8H^2Ad^2O^2,O^2$	Fumaramide.
8	9	1	2	$= C^8H^7Ad,O^2$	Butyramide.
8	8	2	4	$= C^8H^4Ad^2O^2,O^2$	Succinamide.
34	35	1	2	$= C^{34}H^{33}Ad,O^2$	Margaramide.
8	8	2	6	$= C^8H^6AdNO^4,O^2$	Asparagin.
10	6	2	2	$= C^{10}H^2Ad^2,O^2$	Pyromucamide.
12	12	2	12	$= C^{12}H^8Ad^2O^{10},O^2$	Mucamide.
14	7	1	2	$= C^{14}H^5Ad,O^2$	Benzamide.
14	7	1	4	$= C^{14}H^5AdO^2,O^2$	Salicylamide.
16	6	1	5	$= C^{16}H^4AdO^3,O^2$	Phthalamide.
16	7	2	3	$= C^{16}H^5AdNO,O^2$	Amasatin.
28	11	1	4	$= C^{28}H^9AdO^2,O^2$	Benzimide.
40	19	1	16	$= C^{46}H^{17}AdO^{14},O^2$	Opiammon.

The following likewise contain chlorine in the nucleus:

$C^4Cl^3H^2NO^2 = C^4Cl^3Ad,O^2$		Chloracetamide.
$C^{12}Cl^2H^4N^2O^4 = C^{12}Cl^2Ad^2O^2,O^2$		Chloranilamide.

6. *Aldides of Nitro-nuclei.*

$C^{12}H^4N^2O^{10} = C^{12}H^4X^2,O^2$		Nitrophenessic acid.
$C^{12}H^3N^3O^{14} = C^{12}H^3X^3,O^2$		Nitrophenissic acid.
$C^{14}H^7NO^6 = C^{14}H^7X,O^2$		Nitranisol.
$C^{14}H^6N^2O^{10} = C^{14}H^6X^2,O^2$		Binitranisol.
$C^{14}H^5NO^8 = C^{14}H^5XO^2,O^2$		Nitrosalicylous acid.
$C^{16}H^5NO^8 = C^{16}H^5XO^2,O^2$		Nitrophthalanhydride.
$C^{14}H^6N^2O^8 = C^{14}H^4AdXO^2,O^2$		Anilamide.

Most aldides are crystalline; many are oily; a few, like aldehyde, form thin liquids. The tendency to assume the solid state increases with the number of carbon-atoms, and likewise with the proportion of iodine, bromine, chlorine, amidogen, and hyponitric acid.

Most aldides are neutral, provided no formation of acid has taken place in them.

But many of them, even in their original state, redden litmus, and exhibit their acid character by forming saline compounds with bases, the combination being sometimes attended with the elimination of 1 At. water. Such is the case with phenous acid, together with its modifications formed by substitution of bromine, chlorine, or hyponitric acid, viz., salicylous acid, nitrosalicylous acid, and caryophyllic acid.—Bromine, chlorine, or hyponitric acid in the nucleus, appears to exalt the acid character; at least, we are led to suppose so by comparing phenous acid with the acid

formed from it by replacing part of its hydrogen by bromine, chlorine, or hyponitric acid.

Most of these acid aldides, however, are distinguished, according to Gerhardt's observation, from other acids, by not forming ethers of the third class with wood-spirit, alcohol, or fusel-oil, and by combining with 2 At. sulphuric acid to form monobasic copulated acids; whereas, according to Gerhardt's law (p. 222), other monobasic acids, in combination with 2 At. sulphuric acid, produce bibasic acids. It would perhaps be advisable to distinguish those aldides which behave like acids, by the affix *ous*, as, in fact, we do in the case of salicylous acid; according to this rule, we should say phen*ous* instead of phen*ic* acid, &c.

On the other hand, the aldides of the amidogen-nuclei exhibit rather a basic character, which is especially remarkable in the case of urea. Another property by which these aldides are distinguished is, that sometimes when heated with water, sometimes when acted upon by fixed alkalis, acids, &c., they take up an additional quantity of oxygen and hydrogen, and are resolved into ammonia and the (usually acid) compound, from which they were originally produced by the action of ammonia.

β. Compounds of the Nuclei with 4, 6, or 8 At. Oxygen. Monobasic, Bibasic, and Terbasic Acids.

Organic Acids, properly so called.

All compounds of a nucleus with 4, 6, or a greater number of organic atoms, exhibit the properties of fully developed acids. But besides these, there are two other classes of organic acids, viz., the acid aldides, and nuclei analogous to the hydrogen acids, *e. g.*, hydrocyanic acid.

Many organic acids, properly so called, occur in nature, and more abundantly in the vegetable than in the animal kingdom; many others are produced artificially, *e. g.*, in the decomposition of other organic compounds by dry distillation; in the alterations produced in such compounds by the air, and by nitric, chromic, or sulphuric acid, fused hydrate of potash, boiling potash-ley, water, &c.

Most organic acids are entirely composed of carbon, hydrogen, and oxygen, and, inasmuch as they chiefly originate in the vegetable kingdom, or are produced artificially from vegetable substances, they are frequently called *Vegetable-acids*. Among them are several possessing the acid character in the most marked degree; so that, in their affinity to salifiable bases, they are not inferior to the strongest mineral acids, and like the latter, exert a poisonous action when concentrated; *e. g.*, Oxalic acid. Their acid character is stronger in proportion as a smaller number of carbon and hydrogen atoms enter into the composition of the nucleus with which the 4 or 6 external atoms of oxygen are combined, and also as a larger number of hydrogen-atoms in the nucleus are replaced by oxygen. As the number of carbon and hydrogen atoms in the nucleus increases, the acids become weaker; so that at length they lose their sour taste and solubility in water, scarcely redden litmus, and may even be separated from their bases by the action of carbonic acid. Those which contain a considerable amount of oxygen are heavier than water, the specific gravity increasing with the number of oxygen-atoms; whereas those which are comparatively rich in carbon and hydrogen, float upon water. A few of them, at the temperature of 0° are watery, syrupy, or

oily liquids; *e.g.*, formic, lactic, butyric, and oleic acid; but the greater number are solid, and generally crystalline, and most of them fuse before decomposing. Nearly all organic acids are colourless. They are, for the most part, volatile without decomposition, and volatilize with greater facility in proportion as they contain a smaller number of elementary atoms, and as the number of oxygen-atoms among them is less predominant.

Other organic acids contain nitrogen, sometimes existing as such, sometimes as amidogen, sometimes as hyponitric acid. Some acids, such as uric acid and cholic acid, in which the nitrogen exists as such, are produced by natural processes in the animal economy, and are called *Animal acids;* others, such as anthranilic, isatinic, and aspartic acid, are formed by heating other nitrogenous compounds with hydrate of potash or potash-ley. Their acid character is always very feeble. They are crystalline, colourless, and do not volatilize undecomposed.

Amidogen-acids, or *Amidated acids*, are produced either when 1 At. hydrogen in a non-azotized bibasic acid is replaced by amidogen, the change being produced by the action of ammonia (pp. 140—145), or when 4 At. oxygen in a monobasic nitro-acid, are replaced by 2 At. hydrogen (p. 75). These acids, even when formed from a bibasic acid, are themselves monobasic, and exhibit but feeble acid characters. When an amidated acid, formed by the action of ammonia, is boiled with aqueous potash, ammonia is evolved, and the original acid is reproduced in the form of a potash-salt.

Nitro-acids are produced by treating other acids with nitric acid, 1 At. hydrogen being replaced by 1 At. hyponitrous acid, and the acid remaining monobasic or bibasic as before. They are generally yellow and bitter, and rarely volatilize without decomposition. When suddenly heated, they deflagrate with more or less violence, especially after combination with fixed bases.

The common character of all these acids, as indeed of all others, consists in their power of combining with salifiable bases, the combination being attended with more or less complete neutralization of the properties of both the combining substances.

With regard to the proportions in which they combine with bases, these acids, like the inorganic acids, are divided into monobasic, bibasic, and terbasic (II., 7). According to this, 1 At. of a monobasic acid requires to form a normal salt, 1 At. of ammonia or of a metallic oxide composed of MO or M^2O; 1 At. of a bibasic acid requires 2 At., and 1 At. of a terbasic acid requires 3 At. of such a base for the same purpose.

After Graham had demonstrated the existence of monobasic, bibasic, and terbasic phosphoric acid, Liebig in 1838 (*Ann. Pharm.* 26, 113) first showed that many organic acids ought likewise to be regarded as polybasic; viz., fulminic, itaconic, tartaric, tartralic, tartrelic, malic, aspartic, mucic, comenic, and gallic acids as bibasic; and cyanuric, cyanylic, citric, meconic, and tannic acids as terbasic. To these catalogues many other acids have since been added.

Laurent, according to *Th.* 1 (p. 147), supposes that every monobasic acid contains 4 atoms, and every bibasic acid 6 atoms of oxygen external to the nucleus; hence he assigns to benzoic acid the formula $C^{14}H^6,O^4$, and to camphoric acid, $C^{20}H^{16}O^2,O^6$. According to the same view, a terbasic acid must be supposed to contain 8 At. oxygen outside the nucleus; *e.g.*, meconic acid must be expressed by the formula $C^{14}H^4O^6,O^8$.—But we

may also, according to *Th.* 2 (p. 147), suppose that a number of hydrogen-atoms, equal to the number of atoms of base which the acid saturates, are situated outside the nucleus; and accordingly we may express benzoic acid by the formula $C^{14}H^5O,HO^3$, camphoric acid by $C^{20}H^{14}O^4,H^2O^4$, and meconic acid by $C^{14}HO^9,H^3O^5$. In the ordinary metallic salts of these acids, the 1, 2, or 3 At. hydrogen outside the nucleus are replaced by an equal number of atoms of metal. The arguments for and against these two views have already been stated (pp. 20, 21, and 31—37). The latter view forms a transition to Liebig's suggestion, to consider these acids as hydrogen-acids; that is to say, as compounds of radicals with 1, 2, or 3 At. H. According to this view, the three acids just mentioned will be denoted by $C^{14}H^5O^4,H$; $C^{20}H^{14}O^8,H^2$; and $C^{14}HO^{14},H^3$.

It is difficult to decide with any degree of certainty whether the formula of an acid should be so written as to make the acid monobasic, or twice as great so as to make it bibasic, or three times as great so as to make it terbasic. Ought oxalic acid, for example, to be regarded as monobasic$=C^2HO^4\,(C^2H,O^4)$, or as bibasic$=C^4H^2O^8\,(C^4H^2O^2,O^6)$? Is cyanuric acid monobasic$=C^3NHO^2$, or terbasic$=C^6N^3H^3O^6$? The following are the principal considerations by which such questions must be decided.

1. *Entire Atoms.*—An atom of an acid must not be supposed to contain fractions of atoms of the elements. Citric acid dried as completely as possible *per se*$=C^{12}H^8O^{14}$; in the hypothetically anhydrous state t is$=C^{12}H^5O^{11}$. But according to these formulæ, it is terbasic. To make it monobasic, we must divide the formulæ by 3, and assign to the acid dried *per se* the formula $C^4H^{2\frac{2}{3}}O^{4\frac{2}{3}}$, and to the hypothetically anhydrous acid, the formula $C^4H^{1\frac{2}{3}}O^{3\frac{2}{3}}$. The acid is therefore terbasic. (Liebig.) Similarly meconic acid, considered as terbasic, is $C^{14}H^4O^{14}$, and in the hypothetically anhydrous state, $C^{14}HO^{11}$; formulæ which do not admit of division. (Liebig.) Similarly, aspartic acid, $C^8H^7NO^8$ is bibasic, according to Liebig (but according to W. Henry, it is not): to divide the formula by 2 would introduce half-atoms of H and N.

2. *Even numbers of Atoms.*—Since it appears from other phenomena that other organic compounds always contain even numbers of carbon-atoms, we may perhaps be justified in regarding as bibasic those acids which would form exceptions to this law, if they were considered to be monobasic, provided that such an assumption is not forbidden by more important considerations. Such is the case with mesoxalic acid, C^3HO^5, croconic acid, C^5HO^5, pyrotartaric acid, $C^5H^4O^4$, itaconic and citraconic acid, $C^5H^3O^4$, gallic acid, $C^7H^3O^5$, &c.—But uneven numbers of hydrogen and oxygen-atoms, as they rarely occur, may also lead to a duplication of the atom of the acid, if such an alteration of the formula be sanctioned by other reasons; *e.g.*, oxalic acid, C^2HO^4, mellitic acid, C^4HO^4, malic acid, $C^4H^3O^5$, tartaric acid, $C^4H^3O^6$, succinic acid, $C^4H^3O^4$, mucic acid, $C^6H^5O^8$, &c.

3. *Boiling Point.*—The boiling point of a compound may be approximately calculated from its composition (pp. 55—63). Hence, when the boiling point of an acid is known, the number of its elementary atoms may be fixed at that amount which accords best with the boiling point.

If oxalic acid be regarded as monobasic$=C^2HO^4$, and compared with formic acid$=C^2H^2O^4$, which boils at 99°, and differs from oxalic acid only by containing 1 At. hydrogen more, the boiling point of oxalic acid should be $99° + 7{\cdot}5 = 106{\cdot}5$, since, according to Gerhardt's law, the subtraction

of 2H raises the boiling point 15°. But oxalic acid does not boil till it is heated to 212° C; and since part of it is at the same time volatilized in the decomposed state, its true boiling point must be still higher. This circumstance tends to show that oxalic acid is not monobasic. If on the other hand we regard it as bibasic=$C^4H^2O^2,O^6$, and calculate its boiling point as explained on page 61, we find that C^4H^2 gives −15°; 2O in the nucleus, 25°; and 6O outside the nucleus, either 200° or 250°; and thus the calculated boiling point of oxalic acid appears to be either 210° or 260°, which is nearer to the observed boiling point than that given by the former calculation.

Since tartaric acid, when suddenly heated to a temperature between 200° and 300°, boils and undergoes *complete* decomposition, its true boiling point must be considerably higher. The following are the calculated results, according as the acid is regarded as monobasic or bibasic:

Monobasic = $C^4H^4O^2,O^4$		Bibasic = $C^8H^6O^6,O^6$	
C^4H^4	− 12·5°	C^8H^6	+ 25°
2O within	+ 25°	6O within	150°
4O without	150°	6O without, at most	250°
Boiling point	152·5°	Boiling point	425°

Hence tartaric acid, and also racemic acid, which is isomeric with it, and behaves in a precisely similar manner when heated, must be regarded as bibasic.

Mellitic acid bears a heat above 200° without volatilizing or decomposing. If monobasic, its formula is C^4H,O^4; if bibasic, it is $C^8H^2O^2,O^6$. In this case also, calculation shows that the latter formula is the right one:

C^4H	− 7·5°	C^8H^2	+ 55°
4O without	+150°	2O within	25°
	142·5°	6O without, at most	250°
			330°

In the case of pyrotartaric acid, which boils at 188° with slight decomposition, the calculated boiling point does not exceed 137·5°, if the formula be taken as C^5H^4,O^4; but it is at least 220°, if we start from the formula $C^{10}H^8O^2,O^6$, and reckon only 150° for the 6 At. O external to the nucleus.

The boiling points of the other doubtful acids being still less known than those of the acids just considered, the method here exhibited cannot be applied to them.

4. *Relation to Salifiable Bases.—a.* Bibasic acids have a stronger tendency than monobasic acids, to form, not only normal salts in which 2H are replaced by 2 At. metal, but also acid salts in which only 1H is replaced by 1 At. metal. Such salts are formed chiefly with ammonia, potash, soda, baryta, strontia, lime, magnesia, and oxide of silver. (Liebig.) There are, however, many bibasic acids which do not form these acid salts.

b. Bibasic acids have also a greater tendency to form double salts, inasmuch as 1 At. H may be replaced by one metal, and the remaining atom by another metal (or one atom of water by one metallic oxide, and the remaining atom of water by another metallic oxide). Hence an acid salt of a bibasic acid often takes up another metal, and is thereby converted into a normal salt. It is considered to be peculiarly characteristic of bibasic acids that they form double salts with two very similar bases; *e. g.*, tartaric acid with potash and soda, or potash and ammonia.

c. Hagen's law (*Ann. Pharm.* 38, 257)—that if a salt of any acid which is supposed to be monobasic, be found capable of uniting with half an atom of water, the atomic weight of that acid must be doubled—is inadmissible; for crystallized acetate of strontia is $C^4H^3SrO^4+\frac{1}{2}HO=SrO,C^4H^3O^3+\frac{1}{2}HO$; and nevertheless the doubling of the atomic weight of acetic acid is most decidedly forbidden by all the other relations of that acid. In such a case we must suppose that 2 atoms of the dry acetate unite with 1 At. water. (Fresenius.)

d. Neither does Gerhardt's law, that only bibasic acids are capable of yielding amidated acids, assist us in determining whether an acid is monobasic or bibasic; because, for example, in the transformation of oxalic into oxamic acid, we may just as well suppose that 2 At. oxalic acid (regarded as monobasic), when acted upon by ammonia, unite in the formation of 1 At. oxamic acid; and, moreover, it has lately been shown that even a decidedly monobasic acid may be converted into an amidated acid (though not exactly by the action of ammonia)—*e.g.*, benzoic acid, $C^{14}H^6,O^4$ into benzamic acid, $C^{14}H^5Ad,O^4$.

On the subject of polybasic acids, *comp.* Liebig (*Ann. Pharm.* 26, 113, and *Chim. organ.* 1, 6—11); Fresenius (*Ann. Pharm.* 53, 237); Gerhardt (*Compt. mensuels.* 1851, 129).—¶ Gerhardt, in the paper last quoted, extends the above-explained notions regarding the basicity of acids to all acids whatever, inorganic as well as organic. He gives as the definition of an acid: "Any substance which contains hydrogen capable of being replaced by metals by double decomposition,"—the acid being monobasic, bibasic, &c., according as 1, 2, &c., atoms of hydrogen are replaceable by metals. According to this definition, water $\left.\begin{matrix}H\\H\end{matrix}\right\}O$ (*equivalents*, p. 27) is a bibasic acid, and alcohol $\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O$, a monobasic acid (*comp.* p. 17). Sulphuric acid, SO^4H^2—which contains 2 At. of basic hydrogen, and forms two classes of salts; viz., acid salts, such as $\left.\begin{matrix}K\\H\end{matrix}\right\}SO^4$, and neutral salts, such as $\left.\begin{matrix}K\\K\end{matrix}\right\}SO^4$—is bibasic; whereas nitric acid, NO^3H, which contains but one atom of basic hydrogen, and does not form acid salts, is monobasic. In determining the basicity of an acid by this character, however, it is necessary to observe that acid salts may be formed by the combination of a neutral salt of a monobasic acid with the hydrated acid itself; *e.g.*, acid acetate of potash, $C^2H^3KO^2+C^2H^4O^2$, just as basic salts are formed by the union of a neutral salt with a metallic oxide; *e.g.*, basic sulphate of copper$=SO^4Cu^2+Cu^2O$ (p. 208).

For determining the basicity of acids, Gerhardt gives the following characters, not as perfectly absolute, but as sufficiently decisive in the majority of cases:

1. A *monobasic acid* does not form acid salts by double decomposition. It forms but one ammoniacal salt; one neutral mono-alcoholic ether, such as $AcH,C^2H^6O-H^2O$ (Ac denoting the radical of the acid); and one neutral amide of the form AcH,NH^3-H^2O. The volatile organic acids are in general monobasic. The formula which represents their molecule corresponds to 2 volumes, that of water being H^2O.

2. *Bibasic acids* may form with a metal two salts, one acid and the other neutral; with ammonia, an acid and a neutral salt; an acid amide, or monobasic amidogen-acid, of the form $Ac\left\{\begin{matrix}H,NH^3-H^2O\\H\end{matrix}\right\}$, the H being

basic, and a bi-amidated neutral amide = $Ac\left\{\begin{matrix}H,NH^2-H^2O\\H,NH^2-H^2O\end{matrix}\right\}$. With the alcohols they form an acid ether, or monobasic vinic acid = $Ac\left\{\begin{matrix}H,C^2H^6O-H^2O\\H\end{matrix}\right\}$, and a bi-alcoholic neutral ether, such as $Ac\left\{\begin{matrix}H,C^2H^6O-H^2O\\H,C^2H^6O-H^2O\end{matrix}\right\}$

3. Terbasic acids may form with the same acid, three salts, two of which are acid, and the third neutral; with ammonia and the organic alkaloids, three salts and three amides; with the alcohols, three ethers, one of which is ter-alcoholic and neutral, having the form $Ac\left\{\begin{matrix}H,C^2H^6O-H^2O\\H,C^2H^6O-H^2O\\H,C^2H^6O-H^2O\end{matrix}\right\}$, while the other two are acid, the second containing 1 At. and the third 2 At. of basic hydrogen.

Williamson, as already noticed (p. 17), regards all acids, salts, &c., as formed on the type of water, H^2O,—a monobasic acid, such as nitric acid being formed by the substitution of a certain radical, such as NO^2, for 1 At. H in 1 At. of water, giving the formula $\left.\begin{matrix}NO^2\\H\end{matrix}\right\}O$; and a bibasic acid, by the substitution of 1 At. of a radical for 2 At. hydrogen in 2 At. of water; *e.g.*, sulphuric acid $=\left.\begin{matrix}SO^2\\H^2\end{matrix}\right\}O^2$. According to this notation, acid sulphate of potash is $\left.\begin{matrix}SO^2\\HK\end{matrix}\right\}O^2$, and the neutral sulphate, $\left.\begin{matrix}SO^2\\K^2\end{matrix}\right\}O^2$. Anhydrous acids are formed by the replacement of all the hydrogen in 1 or 2 atoms of water by the same radicals: thus, anhydrous nitric acid $=\left.\begin{matrix}NO^2\\NO^2\end{matrix}\right\}O=N^2O^5$; anhydrous sulphuric acid $=\left.\begin{matrix}SO^2\\SO^2\end{matrix}\right\}O^2=S^2O^6$. In short, the anhydrous acids are to the hydrated acids just as ethers are to alcohols.

Gerhardt has adopted this mode of representing the organic acids whose anhydrides he has lately discovered. Thus, hydrated benzoic acid, $=C^7H^6O^2$, is represented as water in which 1 At. H is replaced by benzoyl, $C^7H^5O=Bz$, giving the formula $\left.\begin{matrix}Bz\\H\end{matrix}\right\}O$, and the anhydrous acid or anhydride by $\left.\begin{matrix}Bz\\Bz\end{matrix}\right\}O=C^{14}H^{12}O^3$. The process by which Gerhardt has formed this anhydride, viz., by the action of chloride of benzoyl on benzoate of soda, is similar to that by which Williamson obtained common ether by the action of iodide of ethyl on ethylate of potassium; for just as

$$\left.\begin{matrix}Et\\K\end{matrix}\right\}O \text{ and } EtI \text{ yield } KI \text{ and } \left.\begin{matrix}Et\\Et\end{matrix}\right\}O,$$

so likewise

$$\left.\begin{matrix}Bz\\Na\end{matrix}\right\}O \text{ and } BzCl \text{ yield } NaCl \text{ and } \left.\begin{matrix}Bz\\Bz\end{matrix}\right\}O.$$

Gerhardt has likewise succeeded in preparing some of the compound anhydrous organic acids, analogous to Williamson's compound ethers: thus, the compound C^2H^3O,Cl, and dry benzoate of soda, yield a substance which may be called *acetic benzoate* or *benzoic acetate*, $C^9H^8O^3$: thus

$$\left.\begin{matrix}C^7H^5O\\Na\end{matrix}\right\}O+C^2H^3O,Cl=NaCl+\left.\begin{matrix}C^7H^5O\\C^2H^3O\end{matrix}\right\}O.$$

In a similar manner, *acetic cuminate* $=(C^2H^3O)(C^{10}H^{11}O)O$, *benzoic cuminate* $=(C^7H^5O)(C^{10}H^{11}O)O$, and *benzoic cinnamate* $=(C^7H^5O)(C^9H^7O)O$

have been obtained. Benzoic acetate distilled at 150° yields, by double decomposition, anhydrous acetic acid (acetic acetate) and anhydrous benzoic acid (benzoic benzoate): thus,

$$\left.\begin{matrix}C^2H^3O\\C^7H^5O\end{matrix}\right\}O + \left.\begin{matrix}C^2H^3O\\C^7H^5O\end{matrix}\right\}O = \left.\begin{matrix}C^2H^3O\\C^2H^3O\end{matrix}\right\}O + \left.\begin{matrix}C^7H^5O\\C^7H^5O\end{matrix}\right\}O.$$

(*Ann. Pharm.* 83, 112.) ¶

The following tabular view of the best known monobasic, bibasic, and terbasic acids, is formed upon the principles above explained.

A. Monobasic Acids.

a. Monobasic Acids with Primary Nuclei.

1. *The nucleus containing equal numbers of atoms of Oxygen.*

C	H	O		Melting Point.	C	H	O		Melting Point.
2	2	4	Formic acid		27	27	4	Cocinic acid*	35°
4	4	4	Acetic acid		28	28	4	Myristic acid	49°
6	6	4	Propionic acid		30	30	4	Benic acid	43°
8	8	4	Butyric acid		32	32	4	Ethalic or Cetylic and Palmitic acid	55° & 60°
10	10	4	Valerianic acid						
12	12	4	Caproic acid		34	34	4	Margaric acid	58°
14	14	4	Œnanthylic acid		35	35	4	Stearophanic acid*	68°
16	16	4	Caprylic acid		36	36	4	Bassic acid	70·5°
18	18	4	Azoleic or Pelargonic acid		38	38	4	Stearic acid†	70°
					42	42	4	Behenic acid	78°
20	20	4	Capric acid	18°	54	54	4	Cerotic acid	77·2°
22	22	4	Margaritic acid		60	60	4	Melissic acid	88·9°
24	24	4	Laurostearic acid	43°	68	68	4	Ceric acid (?)†	65°

As the boiling point of these acids rises with the increase of the number of atoms in the nucleus, so likewise does the melting point; the only exceptions are presented by cocinic, stearic, cerotic, and ceric acids, *comp.* Dumas (*Compt. rend.* 5, 935; also *Ann. Pharm.* 45, 330; also *J. pr. Chem.* 28, 330).—Laurent (*Compt. rend.* 21, 852).

According to Redtenbacher (*Ann. Pharm.* 50, 50), the solubility of the baryta-salts of these acids in water likewise increases with the multiple of C^2H^2, which they contain.

2. *The nucleus containing an excess of Carbon-atoms.*

C	H	O		C	H	O	
4	2	4	Maleic acid.	20	12	4	Cuminic acid.
6	4	4	Acrylic acid.	20	18	4	Campholic acid.
10	8	4	Angelicic acid.	30	24	4	Acid from linseed oil.
12	4	4	Metagallic acid (?).	30	28	4	Moringic acid.
12	10	4	Pyroterebic acid.	36	34	4	Oleic and Elaidic acid.
14	6	4	Benzoic acid.	40	30	4	Pinic and Syloic acid.
14	8	4	Pyroguiacic acid.	28	12	5	*Acide stilveux.*
18	8	4	Cinnamic acid.	28	12	6	Benzilic acid.

* Laurent assigns to Cocinic acid the formula $C^{26}H^{26}O^4$, and to Stearophanic acid the formula $C^{36}H^{36}O^4$.

† According to Gerhardt's supposition, which however is not borne out by experiment,—¶ The formula $C^{38}H^{38}O^4$ properly belongs to Balenic acid; and, according to the most trustworthy experiments, Stearic acid is bibasic and polymeric with margaric acid, its formula being $C^{68}H^{68}O^8$. ¶

The two last-mentioned acids form at present an exception to the rule that monobasic acids contain 4O external to the nucleus; similarly with œnanthic acid = $C^{14}H^{13}O^3$.

b. Monobasic Acids with Oxygen-nucleus.

Nucleus. (C	H	O)	O		Nucleus. (C	H	O)	O	
6	4	2	4	Pyroracemic acid.	16	8	2	4	Anisic acid.
6	6	2	4	Lactic acid.	18	8	2	4	Cumaric acid.
8	6	2	4	Glucic acid (?).	18	10	4	4	Veratric acid.
10	4	2	4	Pyromeconic and Pyromucic acids.	20	10	6	4	Opianic acid.
					40	36	2	4	Lithofellic acid.
12	8	2	4	Guiacic acid.	40	12	8	4	Humic acid (?).
14	6	2	4	Salicylic and Ampelic acids.	40	14	8	4	Ulmic acid (?).
14	10	4	4	Terebic acid.	28	10	2	5	*Acide stilbeseux.*

In this list also, *Acide stilbeseux* with its 5O forms an exception to the general law.

c. Monobasic Acids with Chlorine- or Bromine-nucleus.

Nucleus. (C	H	Cl)	O		(C	H	ClBrO)	O	
4	3	1	4	Chloracetic acids.	14	5	1 2	4	Chlorosalicylic acid.
4	1	3	4		14	4	2 2	4	Bichlorosalicylic acid.
8	6	2	4	Chlorobutyric acids.	14	5	1 2	4	Bromosalicylic acid.
8	4	4	4		14	4	2 2	4	Bibromosalicylic acid.
10	7	3	4	Chlorovaleric acid.	16	7	1 2	4	Bromanisic acid.
					20	5	1 2	4	Chloronaphthalic acid.

d. Monobasic Acids with Azo-, Amidogen-, or Nitro-nucleus.

Nucleus. (C	H	Cl	N	O)	O	
8	7		1	4	4	Aspartic acid (?).
14	7		1		4	Anthranilic acid.
16	7		1		6	Isatinic acid.
4	3		1	2	4 = C^4HAdO^2,O^4,	Oxamic acid.
12	3	2	1	2	4 = $C^{12}HAdCl^2O^2,O^4$,	Chloranilam.
14	7		1		4 = $C^{14}H^5Ad,O^4$,	Benzamic acid.
12	3		3		16 = $C^{12}H^3X^3,O^4$,	Styphnic acid = Oxypicric acid.
14	5		1	4	4 = $C^{14}H^5X,O^4$,	Nitrobenzoic acid.
14	5		1	6	4 = $C^{14}H^5XO^2,O^4$,	Nitrosalicylic acid = Indigotic acid.
16	7		1	6	4 = $C^{16}H^7XO^2,O^4$,	Nitranisic acid.
18	7		1	4	4 = $C^{18}H^7X,O^4$,	Nitrocinnamic acid.

e. Monobasic Acid of an Arsenic-nucleus.

$C^{14}H^5AsO^4$ or $C^4H^3ArO^4$, Cacodylic acid.

B. Bibasic Acids.

a. With Oxygen-nucleus.

Nucleus. (C	H	O)	O		(C	H	O)	O	
4	2	2	6	Oxalic acid.	8	6	2	6	Succinic acid.
6	2	2	6	Mesoxalic acid.	8	6	4	6	Malic acid.
8	2	2	6	Mellitic acid.	8	6	6	6	Tartaric and Racemic acids.
8	4	2	6	Fumaric acid.					

Nucleus. (C	H	O)	O	
10	2	4	6	Croconic acid.
10	6	2	6	Itaconic and Citraconic acids.
10	8	2	6	Pyrotartaric acid.
10	8	4	6	Lipic acid.
12	4	4	6	Comenic acid.
12	10	2	6	Adipic acid.
12	10	10	6	Saccharic, Mucic, and Paramucic acids.
14	4	6	6	Chelidonic acid.
14	6	4	6	Gallic acid.

(C	H	O)	O	
14	6	8	6	Rhodizonic acid (?).
14	12	2	6	Pimelic acid.
14	12	6	6	Kinic acid.
16	6	2	6	Phthalic acid.
16	14	2	6	Suberic acid.
20	10	6	6	Hemipinic acid.
20	16	2	6	Camphoric acid.
20	18	2	6	Sebacic acid.
20	18	4	6	Azelaic acid.
24	16	10	6	Kalisaccharic acid.
68	67	1	6	Stearic acid (?).

b. Bibasic Acids with Chlorine- or Bromine-nucleus.

$C^{12}H^3Cl^2O^2,O^6$, Chloranilic acid.
$C^{28}H^{11}Cl,O^{10}$, *Acide chlostilbavique.*
$C^{28}H^{11}Br,O^{10}$, *Acide brostilbavique.*

The last two acids afford new instances of the anomaly of having too much oxygen outside the nucleus.

c. Bibasic Acids with Azo-nucleus.

$C^6H^2N^2O^6$, Parabanic acid.—$C^8H^7NO^2,O^6$, Aspartic acid (?).

d. Bibasic Acids with Nitro-nucleus.

$C^{16}H^5NO^{12} = C^{16}H^7XO^2,O^6$, Nitrophthalic acid.
$C^{28}H^{11}NO^{14} = C^{28}H^{11}X,O^{10}$, Nitrostilbic acid.

The second of these acids likewise exhibits the anomaly above-mentioned.

It is remarkable that no bibasic acid has a nucleus consisting wholly of carbon and hydrogen; but that the nuclei of all these acids contain oxygen or nitrogen in addition to the carbon and hydrogen.

C. Terbasic Acids.

$C^{12}H^6O^4,O^6$, Aconitic acid.
$C^{12}H^8O^6,O^6$, Citric acid.
$C^{14}H^4O^6,O^6$, Meconic acid.
$C^{18}H^8O^4,O^6$, Tannic acid.
$C^6N^3H^3,O^6$, Cyanuric acid.

Cyanuric acid contains too little oxygen to agree with *Th.* 1 (p. 147), according to which, all terbasic acids should contain 8O external to the nucleus; according to *Th.* 2, it should be written: C^6N^3O,H^3O^5. Perhaps however this deficiency of oxygen may be included among the anomalies exhibited by cyanogen-compounds in general.

Many organic acids when subjected to dry distillation, either alone or in contact with fixed alkalis, are resolved into simple products of decomposition, yielding on the one hand, carbonic acid or water or both together, and on the other, an organic compound sometimes neutral, sometimes acid.

Monobasic acids when distilled *per se* generally volatilize undecomposed; those only which have large atomic weights, or whose nucleus does not consist wholly of carbon and hydrogen, but contains oxygen or nitrogen

in addition, suffer decomposition, which is but partial in most cases, and is attended with the formation of neutral products, or at most of monobasic acids.

On the other hand, many compounds of monobasic acids with one atom of a fixed alkali, are resolved by dry distillation into an alkaline carbonate and a neutral compound generally belonging to the class of ketones (p. 214). Moreover, when the acid is intimately mixed and heated with a large excess of a dry fixed alkali, which induces the formation of the greatest possible quantity of carbonic acid, all the four atoms of oxygen outside the nucleus are employed in the formation of that compound, and the nucleus of the acid *minus* 2 At. carbon passes over (p. 136). The distilled product is either free from oxygen, *i.e.*, if the monobasic acid contains 4 At. O,—or it contains 2 At. O, viz., when the monobasic acid contains 6 At. O (*i.e.*, 2 At. within the nucleus and 4 At. without). (Cahours, *N. Ann. Chim. Phys.* 9, 211.)

A few *bibasic acids* can be sublimed without decomposition: *e.g.*, pyrotartaric acid; but most of them, when distilled *per se*, undergo partial or total decomposition. A few merely give off water, and sublime in the form of anhydrides: *e.g.*, camphoric, phthalic, and succinic acids.

Others give off water and are converted into new acids: Malic acid, $C^8H^6O^{10}$, which is bibasic, gives off 2HO, and is converted, partly into 1 At. of bibasic fumaric acid, $C^8H^4O^8$, partly into 2 At. of monobasic maleic acid, $C^4H^2O^4$.

Others again yield 2 At. carbonic acid and a monobasic acid. Oxalic acid, $C^4H^2O^8$, partly volatilizes undecomposed, and is partly resolved into $2CO^2$ and $C^2H^2O^4$ = formic acid. Comenic acid, $C^{12}H^4O^{10}$, gives off $2CO^2$ and yields a sublimate of pyromeconic acid, $C^{10}H^4O^6$; similarly gallic acid, $C^{14}H^6O^{10}$, yields pyrogallic acid, $C^{12}H^6O^6$.

Mucic acid, $C^{12}H^{10}O^{16}$, gives off $2CO^2$ and 6HO, and yields a sublimate of pyromucic acid, $C^{10}H^4O^6$. Tartaric and racemic acid, $C^8H^6O^{12}$, when submitted to dry distillation, are completely decomposed, yielding among other products, pyroracemic acid, $C^6H^4O^6$ ($=C^8H^6O^{12}-2CO^2-2HO$) and pyrotartaric acid, $C^{10}H^8O^8$ ($=2C^8H^6O^{12}-6CO^2-4HO$).

Phthalic acid, $C^{16}H^6O^8$, distilled with excess of lime, is resolved into $4CO^2$ and benzol, $C^{12}H^6$.

Terbasic acids when subjected to dry distillation exhibit similar relations.—Terbasic cyanuric acid, $C^6H^3N^3O^6$, when thus treated, distils over in the form of 3 At. of monobasic cyanic acid, C^2NHO^2.—Terbasic citric acid, $C^{12}H^8O^{14}$, when gently heated, gives off 2HO, and leaves a residue consisting of aconitic acid, $C^{12}H^6O^{12}$, which is also terbasic; this, however, at a higher temperature gives off $2CO^2$, and yields a distillate of bibasic itaconic acid, $C^{10}H^6O^8$.—Terbasic meconic acid, $C^{14}H^4O^{14}$, when its aqueous solution is boiled for a long time, gives off $2CO^2$, and is converted into bibasic comenic acid, $C^{12}H^4O^{10}$; but when submitted to dry distillation, it gives off $4CO^2$, and a sublimate of monobasic pyromeconic acid, $C^{10}H^4O^6$, into which compound comenic acid is also converted by sublimation, with loss of $2CO^2$.

In all these decompositions of monobasic, bibasic, and terbasic acids, the law laid down by Gerhardt (*N. Ann. Chim. Phys.* 7, 223) holds good: viz., the power of any acid to combine with bases diminishes by 1 At. for every double atom of carbonic acid which it gives off; that is to say: a monobasic acid is converted into a neutral compound by giving off $2CO^2$; a bibasic acid becomes monobasic by loss of $2CO^2$, and neutral by

giving up $4CO^2$; and a terbasic acid becomes bibasic by giving off $2CO^2$, monobasic by loss of $4CO^2$, and neutral by losing $6CO^2$ (phthalic acid). Hence the saturating power of an acid is connected with the number of atoms of carbonic acid which the acid is capable of yielding when subjected to dry distillation, either alone, or in contact with fixed alkalis; a monobasic acid yields at most $2CO^2$, a bibasic acid $4CO^2$, and a terbasic acid $6CO^2$. It may be objected that tartaric acid, which contains 12 At. O, might yield $6CO^2$; but when the acid is decomposed, part of this oxygen is expended in the formation of water.

The loss of 2 or more At. HO weakens the acid nature, but not the saturating power, of an acid: *e.g.*, the conversion of citric into aconitic acid. Even if an acid loses xHO at the same time that it gives off xCO^2, its saturating power is not more diminished than it would be by the loss of xCO^2 alone.

Dumas & Piria (*N. Ann. Chim. Phys.* 5, 253) have thrown out the suggestion—which indeed is supported by numerous considerations—that many polybasic acids may be *Copulated acids* (*Acides conjugués*). In corroboration of this view, they have shown that many polybasic acids, when fused with hydrate of potash, are resolved into a number of simpler acids which unite with the potash. Thus, 1 At. of bibasic tartaric acid yields 1 At. oxalic and 1 At. acetic acid:

$$C^8H^6O^{12} = C^4H^2O^8 + C^4H^4O^4;$$

and 1 At. terbasic citric acid yields 1 At. oxalic and 2 At. acetic acid:

$$C^{12}H^8O^{14} + 2HO = C^4H^2O^8 + 2(C^4H^4O^4).$$

These results likewise accord with Gerhardt's law respecting the saturating power of copulated acids (*q. v.*), which is always less by 1 At. than the sum of the saturating powers of the individual acids composing the copulated acid. Thus 1 At. bibasic oxalic acid with 1 At. monobasic acetic acid forms bibasic tartaric acid ($2+1-1=2$); and 1 At. oxalic acid with 2 At. acetic acid form terbasic citric acid ($2+2-1=3$).

Lastly, in favour of this view may be adduced Robiquet's observation that the dry distillation of citric and tartaric acid, yields acetone, a substance which is scarcely ever obtained excepting by the dry distillation of acetates; hence citric acid probably contains acetic acid ready formed.

On the other hand, it must be remembered that sugar likewise yields acetone; and that many compounds, when subjected to dry distillation, yield acetic acid as a product of decomposition, which then, by the further action of heat, especially in presence of charcoal, may be converted into acetone;—moreover, that many other compounds, both acid and neutral—woody fibre for example—yield oxalic and acetic acid when fused with hydrate of potash, whence we might also infer the pre-existence of oxalic and acetic acid in them.—Hence it appears that the facts adduced in favour of Dumas' theory do not really prove anything; and since there are no less violent methods by which tartaric and citric acid can be converted into oxalic and acetic acid, the older theory, that tartaric and citric acid are simple organic compounds, must be allowed to retain its place. It is the predisposing affinity of the potash which compels the atoms of the tartaric and citric acid to unite in new proportions, thereby producing stronger acids, which are capable of saturating a greater number of atoms of potash.

Gerhardt's supposition also, that many monobasic acids are copulated compounds, formed of two monobasic acids, cannot be admitted, merely

from the result of fusion with hydrate of potash, until more convincing facts are adduced in its favour.

The *Salts of the Organic Acids*, in their utmost state of dryness, are constituted as follows, according to the base-saturating power of the acids, and the acid-saturating power of the bases.*

1. The salts which ammonia forms with a monobasic acid contain, in the perfectly dry state, 1 At. Ammonia + 1 At. Acid, as it exists when dried *per se* = 1 At. Ammonium + 1 At. Acid (dried *per se*) − 1 At. Hydrogen = 1 At. Oxide of Ammonium + Hypothetically anhydrous acid. Acid ammoniacal salts of monobasic acids are rare, and have not been much examined.

With a bibasic acid ammonia forms a normal and an acid salt. The former in the dry state = 2 At. Ammonia + 1 At. Acid (dried *per se*) = 2 At. Ammonium + 1 At. Acid (dried *per se*) − 2 At. Hydrogen = 2 At. Oxide of Ammonium + 1 At. hypothetically anhydrous acid. Thus normal tartrate of ammonia = $2NH^3 + C^8H^6O^{12} = C^8H^4(NH^4)^2O^{12} = 2NH^4O + C^8H^4O^{10}$.—The acid salt = 1 At. Ammonia + 1 At. Acid (dried *per se*) = 1 At. ammonium + 1 At. acid (dried *per se*) − 1 At. hydrogen = 1 At. oxide of ammonium + 1 At. acid, from which only 1 At. water has been expelled. Thus, acid tartrate of ammonia = $NH^3 + C^8H^6O^{12} = C^8H^5(NH^4)O^{12} = NH^4 + C^8H^5O^{11}$.

2. The compounds of basic metallic oxides, MO, with organic acids, may, in the dry state, be regarded, according to the substitution-theory, as the acid dried *per se*, in which 1, 2, or 3 At. hydrogen are replaced by 1, 2, or 3 At. metal, according as the acid is monobasic, bibasic, or terbasic. When these salts are produced by bringing a metallic oxide in contact with an acid, 1, 2, or 3 At. water are given off, being formed from the oxygen of the metallic oxide and the hydrogen of the acid. When, however, certain metals dissolve in aqueous acids with evolution of hydrogen, we may suppose that this hydrogen does not proceed from the water, but is expelled by the metal from the acid itself. This view, formerly proposed by myself, that, in the formation of salts, the hydrogen of the acid is replaced by a metal (p. 26), is likewise preferred by Liebig (*Ann. Pharm.* 26, 113). As many atoms of hydrogen replaceable by a metal as an acid contains, so many atoms of base does it require (according to Liebig) to form a normal salt, and accordingly it is said to be monobasic, bibasic, &c. According to this view, an acid consists of hydrogen replaceable by a metal, together with a radical; thus, according to Liebig, the formula of monobasic pyromeconic acid is $C^{10}H^3O^6,H$; of bibasic comenic acid, $C^{12}H^2O^{10};H^2$; and of terbasic meconic acid, $C^{14}HO^{14},H^3$.

According to the radical theory, on the other hand, an acid perfectly dried *per se*, contains as many atoms of *basic water* as there are atoms of base in the normal salt; and in the formation of the salt, which is likewise to be regarded as a compound of the base with a hypothetically anhydrous acid, the water is driven out by the base. According to this view, the water is an educt, but according to the former view it is a product.

Crystallized benzoic acid, for example, is, according to the substitution-theory, $C^{14}H^6,O^4$ (or $C^{14}H^5O,HO^2$); according to the radical-theory,

* The term *Base-saturating power* denotes the mono-, bi-, or terbasic nature of the acid; Gerhardt calls it *Basicity*; but this term might induce misconception, as it seems rather to refer to the basic nature of a body.

$HO,C^{14}H^5O^3$. Its silver-salt is, according to the former theory= $C^{14}H^5Ag,O^4$ (or $C^{14}H^5O,AgO^3$); for,

$$C^{14}H^6O^4 + AgO = C^{14}H^5AgO^4 + HO.$$

According to the radical-theory, the silver-salt is $AgO,C^{14}H^5O^3$; for,

$$HO,C^{14}H^5O^3 + AgO = AgO,C^{14}H^5O^3 + HO.$$

Benzoate of silver crystallizes in this anhydrous state, even from its aqueous solution; many other salts retain a certain number of atoms of water, which they do not give up till heated to 200° or above; with others again this dehydration is impossible, because the temperature which it requires is above that at which the salts decompose. Thus benzoate of baryta, dried at 100°, retains 1 At. water, and, according to the substitution-theory, may be regarded either as $BaO,C^{14}H^6O^4$, or as $C^{14}H^5BaO^4 + HO$. In fact, it is uncertain whether 1 At. is replaced by 1 Ba in the acid itself, and the HO is attached merely as water of crystallization, or, as is more probable, the crystallized acid is actually combined with the baryta, and substitution does not take place till the water is expelled at a heat above 100°. The latter view is supported by the fact, that the salts may be obtained in the anhydrous state at a lower temperature, in proportion as the metallic oxide more readily gives up its oxygen, and allows it to go off with the hydrogen of the acid in the form of water; hence, in general, silver-salts are most easily brought into the anhydrous state, and next to them the lead-salts. This circumstance is also, as remarked by Liebig, favourable to the substitution-theory and unfavourable to the radical-theory; for since, according to the latter, the metallic oxide replaces the water combined with the hypothetically anhydrous acid, it follows that the fixed alkalis, which have the strongest affinity for acid, should expel the water much more readily than oxide of silver or oxide of lead.

According to the radical-theory also, benzoate of baryta, dried at 100°, may be regarded in two ways, viz., either as $BaO,C^{14}H^5O^3 + Aq.$ or as $BaO + HO,C^{14}H^5O^3$, *i. e.*, either as anhydrous baryta-salt + 1 At. water, or as a compound of baryta with the so-called hydrate of benzoic acid (*i. e.*, the acid dried *per se.*)

That which has been said of benzoate of baryta is true in a still higher degree, of all the numerous salts which cannot be brought into the dry state at any temperature; *e. g.*, many salts of the earthy alkalis and of magnesia.

A *monobasic acid* may form with bases having the formula MO, not only normal but likewise *acid* and *basic salts;* the acid salts, however, are rare. Thus 2 At. margaric acid = $2C^{34}H^{34}O^4$, form with 1 At. potash (1HO being separated), a salt which, according to the substitution-theory, is $C^{34}H^{33}KO^4 + C^{34}H^{34}O^4$, and, according to the radical-theory, $KO,C^{34}H^{33}O^3 + HO,C^{34}H^{33}O^3$.

Basic salts are more common; they contain 2, 3, 4, 6, or more, At. of a base united with 1 At. acid. But in this reaction, only 1 At. water is separated from 1 At. acid, and these salts may be regarded as compounds of an anhydrous normal salt with one or more atoms of a metallic oxide. Thus the tris-acetate of lead is $2PbO,C^4H^3PbO^4 = 3PbO,C^4H^3O^3$.

A *bibasic acid* forms a normal salt with 2 At. base (MO), with separation of 2 At. water, 2H of the acid being replaced by 2 At. metal, according to the nucleus-theory, and 2HO by 2 At. metallic oxide, accord-

ing to the radical-theory. Moreover, many bibasic acids form acid salts with various metallic oxides, as with potash, soda, baryta, strontia, lime, magnesia, oxide of copper, &c. In this case, only 1 At. of oxide enters the acid, and only 1. At. of water is expelled.

In the case of tartaric acid and its two compounds with potash, the formulæ, according to the two theories, are as follows:

	Tartaric acid.	*Acid Potash-salt.*	*Normal Potash-salt.*
Substitution-theory:	$C^8H^6O^{12}$	$C^8H^5KO^{12}$	$C^8H^4K^2O^{12}$
Radical-theory:	$2HO,C^8H^4O^{10}$	$KO,HO,C^8H^4O^{10}$	$2KO,C^8H^4O^{10}$

In the acid salt, the substitution-theory supposes that one of the two replaceable atoms of hydrogen in the acid remains unaltered; according to the radical-theory, one of the separable atoms of water remains.

Bibasic acids often form *double salts*, in which 1 At. H is replaced by one metal, and the remaining At. H by another; or, according to the radical-theory, one At. HO by one metallic oxide, and the remaining At. HO by another oxide. Thus, tartrate of potash and soda = $C^8H^4KNaO^{12}$, or = $KO,NaO,C^8H^4O^{10}$.

Basic salts are rarely formed by bibasic acids; many compounds ordinarily so called ought rather to be regarded in a different manner, as will be further explained in the *special* part of the work.

A terbasic acid exhibits corresponding relations; but inasmuch as it contains 3 At. H replaceable by a metal, or 3 At. of basic water, it is capable, according to circumstances, of forming with the same base, three different kinds of salts, viz., a normal or terbasic, a bibasic, and a monobasic salt; *e. g.*, citric acid with potash:

	Citric acid.	*Monobasic.*	*Bibasic.*	*Terbasic.*
Substitution-theory:	$C^{12}H^8O^{14}$	$C^{12}H^7KO^{14}$	$C^{12}H^6K^2O^{14}$	$C^{12}H^5K^3O^{14}$
Radical-theory:	$3HO,C^{12}H^5O^{11}$	$KO,2HO,C^{12}H^5O^{11}$	$2KO,HO,C^{12}H^5O^{11}$	$3KO,C^{12}H^5O^{11}$

It is remarkable that there are no known salts of organic terbasic acids containing two or three metals, although terbasic phosphoric acid exhibits several such examples.

Metallic oxides of the formula M^2O, such as the grey oxide of mercury, appear to comport themselves with organic acids in the same manner as those which have the formula MO. Thus, for one example, mercurous acetate = $C^4H^3Hg^2O^4$, or $Hg^2O,C^4H^3O^3$. In this case, the substitution-theory obliges us to suppose that 1H is replaced by 2Hg. Further investigation is, however, required.

Those metallic oxides which contain 3 At. of oxygen to 1 or 2 At. of metal, exhibit a different relation to organic acids.

Uranic oxide, U^2O^3, in combining with acetic acid, expels 1 At. water, and forms the anhydrous salt $C^4H^3(U^2O^2)O^4$ or $U^2O^3,C^4H^3O^3$. The first formula does not accord with Peligot's view, that *uranyl* = U^2O^2 is to be regarded as a metalloidal compound (IV. 160).—In the combination of uranic oxide with tartaric acid, no water is expelled; for the salt dried at 200° is composed of $2U^2O^3,C^8H^6O^{12}$. Similarly with oxalic acid. In all these combinations with organic acids, just as in its inorganic compounds, uranic oxide is mono-acid, not ter-acid, although, according to its three atoms of oxygen, it might be expected to require 3 At. of a monobasic acid.

The red and blue double salts which chromic oxide forms with oxalic acid and potash, may be expressed according to the two theories, by the

following formulæ (in the radical-theory, oxalic acid is supposed to be monobasic):

	Blue.	*Red.*
Substitution-theory:	$2(C^4HKO^8) + C^4K(Cr^2O^2)O^8$	$C^4HKO^8 + C^4H(Cr^2O^2)O^8$
Radical-theory:	$3(KO,C^2O^3) + Cr^2O^3,3C^2O^3,2Aq.$	$KO,C^2O^3 + Cr^2O^3,3C^2O^3,2Aq.$

similar therefore to uranic acetate.

Ferric oxide, in combining with most acids, does not appear to drive out water; but with pyromeconic acid, $C^{10}H^4O^6$, it forms a red crystalline salt, which, when dried at 100°, has, according to the radical-theory, the formula $Fe^2O^3,3(C^{10}H^3O^5)$, *i. e.*, 1 At. ferric oxide to 3 At. hypothetically anhydrous pyromeconic acid, and, according to the substitution-theory, the formula $C^{30}H^9Fe^2O^{18}$; this supposes that in 3 At. pyromeconic acid, 3H are replaced by only 2Fe.

Antimonic oxide, in certain double salts, exhibits a remarkable relation, which is most plainly seen in the case of tartar-emetic. The crystallized salt loses 1 At. water at 100°, and 2 At. more when dried for some time in a current of air at 200°. In these two states it has the following composition:

	Crystallized.	*Dried at* 100°.	*Dried at* 200°.
Substitution-theory:	$C^8H^4K(SbO^2)O^{12} + Aq.$	$C^8H^4K(SbO^2)O^{12}$	$C^8H^2KSbO^{12}$
Radical-theory:	$KO,SbO^3,C^8H^4O^{10} + Aq.$	$KO,SbO^3,C^8H^4O^{10}$	$KO,SbO^3,C^8H^2O^8$

In this salt the antimonic oxide enters, like uranic oxide, not as a ter-acid but as a mono-acid base. According to the substitution-theory, one of the replaceable atoms of hydrogen in the salt dried at 100°, is replaced by K, the other by the compound SbO^2, not known in the separate state; and the crystallized salt likewise contains 1 At. of water of crystallization. According to the radical-theory, the two atoms of basic water in the tartaric acid are replaced by 1KO and $1SbO^3$. With regard to the salt dried at 200°, which, when redissolved in water, forms a solution of unaltered tartar-emetic, the substitution-theory must, I think, admit the following explanation: Tartaric acid, $C^8H^6O^{12}$ ($=C^8H^6O^6,O^6$), heated to 180° by itself for a long time, passes, with loss of 2HO, into tartaric anhydride, $C^8H^4O^{10}$ ($=C^8H^4O^8,O^2$), which gradually redissolves in water, yielding a solution of tartaric acid. And as tartar-emetic dried at 100° is tartaric acid in which 2H are replaced by $K(SbO^2)$, so likewise the salt dried at 200°, viz., $C^8H^2K(SbO^2)O^6,O^2$ is tartaric anhydride with the same substitutions. Another explanation would be that the 2HO which go off at 200°, are formed, not from 2O of the acid, but from 2O of the SbO^2; if this be the case, $C^8H^2KSbO^8,O^4$ will remain; but this residue, since it contains 4O without the nucleus, should behave like an acid. The radical-theory does not so readily afford a satisfactory explanation of this change. According to this theory, tartaric acid, in its driest state, is $C^8H^4O^{10}$; hence the salt dried at 200° must be supposed to contain a peculiar acid, $C^8H^2O^8$ (the formula of mellitic acid dried *per se*); and yet when digested in water, it is reconverted into ordinary tartar-emetic, and no evidence whatever can be obtained of the presence of a peculiar acid.—Arsenious acid, AsO^3, behaves with potash and tartaric acid, just like antimonic oxide.

On the other hand, antimonic oxide forms, with terbasic citric acid, $C^{12}H^8O^{14}$, and potash, a salt which, when dried at 190°, may be expressed either by $C^{12}H^7KO^{14} + C^{12}H^7SbO^{14}$, or by $3KO,C^{12}H^5O^{11} + SbO^3$, $C^{12}H^5O^{11}$. In this case, a ter-acid basic unites in equal number of atoms

with a terbasic acid, and all three atoms of oxygen in the base are expelled as water.

Gerhardt denotes all such compounds of organic acids with metallic oxides of the forms M^2O^3 and MO^3, by the term *Emetics* (although, according to the above observations, they often differ from tartar-emetic in every respect).

The salts of organic acids are distinguished from those of inorganic acids by their behaviour in the fire. Some of them, such as the ammoniacal salts of the more volatile acids, evaporate undecomposed; others, such as acetate of alumina, give off the acid in its original state; and a very few, among which may be mentioned cyanate of potash, remain unaltered, even at a red-heat, if kept from the air, but evolve carbonic acid if the air has access to them. But by far the greater number of the salts of organic acids are resolved by dry distillation, sometimes into carbonic acid, water, and more simple organic substances, such as ketones, &c. (p. 136); but sometimes, especially if the heat be suddenly applied, they undergo more complex decompositions, in which they evolve carbonic acid, carbonic oxide, marsh gas, empyreumatic oil, and, in the case of azotized bodies, also carbonate of ammonia, and a small quantity of hydrocyanic acid, and all (excepting the oxalates) leave a coaly residue. In this residue the base may exist in the following states, according to the tenacity with which it retains its oxygen, and the strength of its affinity for carbonic acid; viz., as a carbonate, which is the case with potash; as pure base, *e. g.*, magnesia; as a metal, *e. g.*, copper; and, finally, as a cyanide, as when the compound of a fixed alkali with a nitrogenous acid is ignited out of contact of air. The salts of organic acids are also distinguished by this peculiarity, that many of them, when kept for some time in the state of dilute solution, are decomposed, with formation of carbonic acid, mould, and mucus.

d. Compounds of Nuclei with Sulphur.

These compounds are analogous to those of oxygen, but as their number is but small, it is sufficient to enumerate the principal of them.

A nucleus may combine:

1. With HS, forming a compound corresponding to an ether (and designated in the author's system by the term *Schwefel-afer*).
2. With H^2S^2, corresponding to an alcohol (*Mercaptans*).
3. With HS^2, with HS^3, and with H^2S^4, forming compounds which require further examination.
4. With ClS.
5. With 2 At. sulphur, corresponding to an aldide.
6. With 4 At. sulphur, corresponding to a monobasic acid, but so far as is yet known, not exhibiting acid properties.

C^2H^2,HS	Sulphide of Methyl [Schwefel-Formafer].
C^4H^4,HS	Sulphide of Ethyl [Schwefel-Vinafer].
C^4Cl^4,HS	Quadrochloruretted Sulphide of Ethyl [Falavinek].
C^4H^3Ar,HS	Monosulphide of Cacodyl.
$C^{10}H^{10},HS$	Sulphide of Amyl [Schwefel-Mylafer].
$C\,H^2,H^2S^2$	Methyl-mercaptan.
C^2H^4,H^2S^2	Mercaptan.
CH^{10},H^2S^2	Amyl-mercaptan.

C^2H^2,HS^2	Bisulphide of Methyl.
$C^2H^2,HS^3 = C^2HS,H^2S^2$	Tersulphide of Methyl.
C^4H^9Ar,HS^3	Tersulphide of Cacodyl.
C^2Cl^2,ClS	Sulphide of Chloride of Carbon [Fakaformek].
C^4H^4,S^2	Bisulphide of Ethylene [= Fevine].
$C^{14}H^6,S^2$	Bisulphide of Benzene [= Febunze].
C^4H^4,S^4	Tetrasulphide of Ethylene [= Fovine].

Tellurium, which is an analogue of sulphur, forms the Telluride of Ethyl, C^4H^4,HTe.

e. Compounds of the Nuclei with Iodine, Bromine, Chlorine, or Fluorine.

These elements, if attached externally to the nucleus, take the place of oxygen much more frequently than that of hydrogen. The compounds thus formed exhibit relations analogous to those of the sulphur-compounds. The best known compounds belonging to this class are the following:

Crude Formula.	*Th.* 1.	*Th.* 2.	
$C^4H^4I^2$	$= C^4H^4,I^2$	$= C^4H^3I,HI$	Monioduretted Hydriodic Ether [Schevine].
C^2H^3I	$= C^2H^2,HI$	$= C^2HI,H^2$	Iodide of Methyl [Iod-Formafer].
C^2HI^3	$= C^2HI,I^2$	$= C^2I^2,HI$	Iodoform.
C^4H^5I	$= C^4H^4,HI$	$= C^4H^3I,H^2$	Iodide of Ethyl [Iod-Vinafer].
$C^{10}H^{11}I$	$= C^{10}H^{10},HI$	$= C^{10}H^9I,H^2$	Iodide of Methyl [Iod-Mylafer].
C^2H^3Br	$= C^2H^2,HBr$	$= C^2HBr,H^2$	Bromide of Methyl [Brom-Formafer].
C^2HBr^3	$= C^2HBr,Br^2$	$= C^2Br^2,HBr$	Bromoform.
C^2HI^2Br	$= C^2HBr,I^2$	$= C^2I^2,HBr$	Bromiodoform.
C^4H^5,Br	$= C^4H^4,HBr$	$= C^4H^3Br,H^2$	Bromide of Ethyl or Hydrobromic ether [Brom-Vinafer].
C^4H^4Br	$= C^4H^4,Br^2$	$= C^4H^3Br,HBr$	*or* $C^4H^2Br^2,H^2$, Monobromuretted Hydrobromic ether [Mevine].
$C^{10}H^{11}Br$	$= C^{10}H^{10},HBr$	$= C^{10}H^9Br,H^2$	Bromide of Methyl [Brom-Mylafer].
$C^{16}H^8Br^2$	$= C^{16}H^8,Br^2$	$= C^{16}H^7Br,HBr$	*or* $C^{16}H^6Br^2H^2$, Bromostyrol.
$C^{20}H^6Br^6$	$= C^{20}H^6Br^2,Br^4$	$= C^{20}H^4Br^4,H^2Br^2$	Produced from Napthaline by Bromine.
$C^{20}H^5Br^7$	$= C^{20}H^5Br^3,Br^4$	$= C^{20}H^3Br^5,H^2Br^2$	
$C^{28}H^{12}Br^2$	$= C^{28}H^{12},Br^2$	$= C^{28}H^{11}Br,HBr$	*or* $C^{28}H^{10}Br^2,H^2$, Bromostilbene.
$C^{28}H^{11}Cl,Br^2$	$= C^{28}H^{11}Cl,Br^2$	$= C^{28}H^{10}Br^2,HCl$	*or* $C^{28}H^9ClBr^2,H^2$, *Bromure de Chlostilbase.*
$C^{12}H^5Br^5$	$= C^{12}H^6,Br^5$	$= C^{12}H^3Br^3,H^2Br^3$	Bromobenzene [Maufune].
C^2H^3Cl	$= C^2H^2,HCl$	$= C^2HCl,H^2$	Chloride of Methyl [Chlor-Formafer].
$C^2H^2Cl^2$	$= C^2H^2,Cl^2$	$= C^2HCl,H^2$	*or* C^2Cl^2,H^2, Monochloruretted Chloride of Methyl [Keforme].
C^2HCl^3	$= C^2HCl,Cl^2$	$= C^2Cl^2,HCl$	Chloroform.
C^2HICl^2	$= C^2HI,Cl^2$	$= C^2ICl,HCl$	Chloriodoform.
C^2Cl^4	$= C^2Cl^2,Cl^2$	$= C^2Cl^2,Cl^2$	Bichloride of Carbon [Keformek].
C^4H^5Cl	$= C^4H^4,HCl$	$= C^4H^3Cl,H^2$	Hydrochloric ether, *or* Chloride of Ethyl [Chlor-Vinafer].
$C^4H^4Cl^2$	$= C^4H^4,Cl^2$	$= C^4H^3Cl,HCl$	*or* $C^4H^2Cl^2,H^2$.*
$C^4H^3Cl^3$	$= C^4H^3Cl,Cl^2$	$= C^4H^2Cl^2,HCl$	*or* C^4HCl^3,H^2
$C^4H^2Cl^4$	$= C^4H^2Cl^2,Cl^2$	$= C^4HCl^3,HCl$	*or* C^2Cl^4,H^2 } Hydrochloric ether with Cl substituted for H.
C^4HCl^5	$= C^4HCl^3,Cl^2$	$= C^4Cl^4,HCl$	
C^4Cl^6	$= C^4Cl^4,Cl^2$	$= C^4Cl^4,Cl^2$	Sesquichloride of Carbon [Kevinok].

* This formula belongs to two isomeric compounds, the oil of olefiant gas, and the compound formed from hydrochloric ether by the substitution of 1 At. Cl for 1 At. H. The former is decomposed by potash and alcohol, the latter not; hence the former should perhaps be denoted by one of the first two formulæ; the latter by the third.

Crude Formula.	*Th.* 1.	*Th.* 2.	
$C^{10}H^{11}Cl$	$= C^{10}H^{10},HCl$	$= C^{10}H^{9}Cl,H^{2}$	Chloride of Amyl [Chlor-Mylafer].
$C^{10}H^{5}Cl^{9}$	$= C^{10}H^{2},Cl^{8}HCl$	$= C^{10}HCl^{9},H^{2}$	The same, with H replaced by Cl.
$C^{32}H^{33}Cl$	$= C^{32}H^{32},HCl$	$= C^{32}H^{31}Cl,H^{2}$	Chloride of Cetyl [Chlor-Zitafer].
$C^{14}H^{6}Cl^{4}$	$= C^{14}H^{6}Cl^{2},Cl^{2}$	$= C^{14}H^{5}Cl^{3},HCl$	*or* $C^{14}H^{4}Cl^{4},H^{2}$, Chloride of Toluol.
$C^{20}H^{6}Cl^{4}$	$= C^{20}H^{6}Cl^{2},Cl^{2}$	$= C^{20}H^{5}Cl^{3},HCl$	
$C^{20}H^{6}Br^{2}Cl^{2}$	$= C^{20}H^{6}Br^{2},Cl^{2}$	$= C^{20}H^{5}Br^{2}Cl,HCl$	Compounds obtained from Naphthalin by the action of Chlorine.
$C^{20}H^{7}Cl^{5}$	$= C^{20}H^{7}Cl,Cl^{4}$	$= C^{20}H^{5}Cl^{3}H^{2},Cl^{2}$	
$C^{20}H^{6}Cl^{6}$	$= C^{20}H^{6}Cl^{2},Cl^{4}$	$= C^{20}H^{4}Cl^{4},H^{2}Cl^{2}$	
$C^{14}H^{7}Cl^{5}$	$= C^{14}H^{7}Cl,Cl^{4}$	$= C^{14}H^{5}Cl^{3},H^{2}Cl^{2}$	Obtained from Toluol = $C^{14}H^{8}$ by chlorine [= Kotolak, Kotolik, and Kautolek].
$C^{14}H^{5}Cl^{7}$	$= C^{14}H^{5}Cl^{3},Cl^{4}$	$= C^{14}H^{3}Cl^{5},H^{2}Cl^{2}$	
$C^{14}H^{6}Cl^{8}$	$= C^{14}H^{6}Cl^{2},Cl^{6}$	$= C^{14}H^{3}Cl^{5},H^{3}Cl^{3}$	
$C^{12}H^{6}Cl^{6}$	$= C^{12}H^{6},Cl^{6}$	$= C^{12}H^{3}Cl^{3},H^{3}Cl^{3}$	Chloride of Benzin [Kaufuue].
$C^{2}H^{3}F$	$= C^{2}H^{3},HF$	$= C^{2}HF,H^{2}$	Fluoride of Methyl [Fluor-Formafer].

C. Copulated Compounds.

This term is applied to a peculiar class of compounds, formed by the union of an organic substance with another body, either organic or inorganic, generally with separation of 2, 4, 6, or 8 At. HO. In these compounds the characteristic properties of the two generating substances (*Corps générateurs*) are often completely masked.

A copulated compound is usually regarded as a compound of the two residues left from the two constituent compounds after the removal of a certain number of atoms of water. But the presence of these residues in the copulated compound cannot be discovered by the reactions which they would exhibit in the free state. When the copulated compound is decomposed in presence of water, these residues are not separated in the free state, but take up again the water which they have lost, and are reconverted into the two substances from which they were formed by elimination of water.

Hence it is most probable that, in the formation of the copulated compound, the atoms of the two substances left after separation of the water, attach themselves to each other in such a manner, that the original mode of combination is more or less destroyed, and consequently the substances can no longer exhibit the reactions which formerly belonged to them.

Since, however, nothing is known of the manner in which the atoms of the two residues are united in these copulated compounds, we content ourselves with indicating the two residues in the formula; this, however, must not be understood to imply that the two residues actually exist, as such, in the copulated compound. That residue which exhibits an indifferent character, that is to say, neither acid nor basic, is called the *Copula*.

In the distillation of wood-spirit, $C^{2}H^{4}O^{2}$, with oil of vitriol, HO,SO^{3}, two atoms of water are separated, and sulphate of methyl, $C^{2}H^{3}O,SO^{3}$, passes over. This oil has no acid reaction, and does not precipitate baryta-salts; but in hot water, it is immediately reconverted into wood-spirit and aqueous sulphuric acid. The radical-theory is in error in ascribing to methylic ether, $C^{2}H^{3}O$, supposed to exist in this oil, a basic character, by virtue of which it neutralizes the sulphuric acid; for this $C^{2}H^{3}O$, which is a gas, does not neutralize *dilute* sulphuric acid, and is not even absorbed by it. [For further observations on this point, *vid. Ethers of the third class*, p. 216.] The formula, $C^{2}H^{3}O,SO^{3}$, therefore rests on a

mere fiction. More correct, perhaps, is the formula given by Gerhardt (*Ann. Chim. Phys.* 72, 180), viz., $C^2H^3(SO^3)O^3$, according to which this compound is wood-spirit in which 1H is replaced by $1SO^3$. Another formula by which this compound may be expressed is C^2H^2,HSO^4. We may imagine the atoms C^2H^3, grouped in the form of a square table (p. 37), having 1H attached to its upper and 1S to its under surface, while the 4O are attached to the four edges of the table, so that the sulphuric acid no longer retains its own proper nature, but is merely present in the compound by its elements, and may, therefore, under certain circumstances, be reproduced. It is only because such hypotheses are at present without satisfactory foundation, that the more common and simple formula C^2H^3O,SO^3, is retained, although it by no means expresses the real constitution of the compound.

a. Acetones in general or Ketones.

These compounds are all produced by the dry distillation of different salts, which monobasic acids form with fixed alkalis. This reaction has been already explained (p. 136). In the case of acetic acid, the same decomposition is produced by the mere action of a red heat:

$$2C^4H^4O^4 = C^6H^6O^2 + 2HO + 2CO^2.$$

All ketones are highly combustible, neutral compounds which float upon water volatilize without decomposition, and with the exception of margarone, which is crystalline, are watery or oily liquids.

Chancel (*Compt. rend.* 20, 1580) suggests that ketones are not primary organic compounds, but copulated compounds, made up of the aldide of the acid from which they are produced and a hydrocarbon containing 2C and 2H less than the nucleus of the same acid. Thus:

	C	H	O	= C	H	O	+ C	H
Acetone	6	6	2	4	4	2	2	2
Metacetone *or* Propione	10	10	2	6	6	2	4	4
Butyrone	14	14	2	8	8	2	6	6
Valerone	18	18	2	10	10	2	8	8
Benzone	26	10	2	14	6	2	12	4
Campholone	38	34	2	20	18	2	18	16
Margarone	66	66	2	34	34	2	32	32

If acetone were a primary organic compound, it should be regarded as the aldide of propionic acid, $C^6H^6O^4$, and should be converted into that acid by oxidation with chromic acid, &c.; instead of which it yields a number of other products, and chiefly acetic acid. In a similar manner, when passed in the state of vapour through a hot mixture of lime and hydrate of potash, it yields, according to Gottlieb, acetate and formiate of potash, which corresponds exactly with Chancel's view, since the aldehyde, C^4H^4,O^2, may be thereby converted into acetic acid, and the methylene, C^2H^2, into formic acid. Similarly propione, $C^{10}H^{10}O^2 = C^6H^6O^2 + C^4H^4$, when oxidated by chromic acid, yields, not valerianic acid, but propionic acid, C^6H^6,O^4, and acetic acid, $C^4H^4O^4$. Formic acid cannot yield any peculiar ketone; for, according to the preceding, this compound would be $C^2H^2O^2$ (the unknown aldide of the methylic series) + $C^2H^2 - C^2H^2 = C^2H^2O^2$; that is to say, the ketone of the methylic series would be identical with its aldide. (*comp.* Chancel.)

The ketones may likewise be regarded as compounds of the aldide

of the decomposed acid with the alcohol of the series next below, *minus* 2 At. water; *e. g.*, Acetone = $C^4H^4O^2 + C^3H^4O^2 - 2HO$.*

But all ketones differ in many respects from other copulated compounds; *e. g.*, with regard to their modes of formation and decomposition.

With these ketones may perhaps be classed chlorobutyrone, $C^{14}H^{13}Cl$, which is produced by the action of pentachloride of phosphorus on butyrone, $C^{14}H^{14}O^2$, and is probably $C^8H^8 + C^6H^5Cl$; *i. e.*, a compound of two nuclei in which 1H is replaced by 1Cl. Similarly, with Laurent's *Thionessal*, $C^{26}H^9S$, which may be derived from benzene = $C^{14}H^6 + C^{12}H^3S$.

b. Compound Ethers formed by Oxygen-acids [*Ester*].

Ethers of the Third Class.

Many oxygen-acids, both organic and inorganic, act upon the alcohols in such a manner that water is separated and a neutral volatile ethereal substance formed, which may be regarded as a copulated compound of the alcohol and the acid *minus* water, or according to the radical-theory, as a salt in which an acid is combined with an ether.

A monobasic acid forms an ether of the third class with 1 At. of an alcohol, 2 At. water being separated (*comp.* pp. 201, 201). If however a mineral acid be supposed to be in the anhydrous state, only 1 At. water will be separated.

Thus alcohol, $C^4H^6O^2$, repeatedly distilled with acetic acid, $C^4H^4O^4$, yields 2 At. water and 1 At. acetic ether = $C^8H^8O^4$. An attempt to explain the manner in which the atoms arrange themselves in this formation of the compound ether, has already been given (p. 35). For the instance of wood-spirit and sulphuric acid, *vid.* p. 214.

When a bibasic organic acid forms a compound ether, 2 At. of alcohol unite with 1 At. of the acid, with separation of 4 At. water. Thus, with succinic acid:

$$2C^4H^6O^2 + C^8H^6O^8 - 4HO = C^{16}H^{14}O^8.$$

If only 1 At. of the alcohol were to unite with 1 At. of the bibasic acid, the resulting compound would be a copulated monobasic acid.

Lastly, 1 At. of a terbasic organic acid requires 3 At. of an alcohol, and 6 At. water are eliminated in the reaction. Thus, with aconitic acid:

$$3C^4H^6O^2 + C^{12}H^6O^{12} - 6HO = C^{24}H^{18}O^{12} = 3C^4H^6O, C^{12}H^3O^9.$$

Of the 2HO produced from a monobasic acid in the formation of an

* They may also be regarded as salts formed from the aldides by the substitution of the *radical* of the next lowest series for 1 At. hydrogen, *e.g.*:

$$\text{Aldehyde} = C^4\left\{\begin{matrix}H^3\\H\end{matrix}\right\}O^2; \quad \text{Acetone} = C^4\left\{\begin{matrix}H^3\\C^2H^3\end{matrix}\right\}O^2.$$

A similar view may be given of the compound or intermediate ketones discovered by Williamson (p. 137); thus, the compound, $C^{12}H^{12}O^2$, obtained by heating a mixture of acetate of soda and valerate of potash, may be regarded as the methyl-salt of valeric aldide, $C^{10}\left\{\begin{matrix}H^9\\C^2H^3\end{matrix}\right\}O^2$; or as the butyl-salt of common aldehyde, $C^4\left\{\begin{matrix}H^3\\C^8H^9\end{matrix}\right\}O^2$; or adopting the formulæ and atomic weights used by Williamson and Gerhardt:

$$\text{Aldehyde} = \left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}; \quad \text{Acetone} = \left.\begin{matrix}C^2H^3O\\CH^3\end{matrix}\right\};$$

$$\text{Intermediate Ketone} = \left.\begin{matrix}C^5H^9O\\CH^3\end{matrix}\right\} = \left.\begin{matrix}C^2H^3O\\C^4H^9\end{matrix}\right\}.$$

(Williamson, *Chem. Soc. Qu. J.* 4, 234; Gerhardt, *Ann. Pharm.* 83, 115.) [W.]

ether of the third class, 1H and 1O are probably derived from the alcohol, and the rest from the acid. When the acid is bibasic, 2 At. alcohol yield 2H and 2O, and the acid likewise 2H and 2O; and similarly with a terbasic acid.

According to Gerhardt, on the contrary (pp. 75, 76), all the H of the water produced proceeds from the alcohol, and all the O from the acid. Thus, for example, his alcohol-residue = $C^4H^6O^2 - H^2 = C^4H^4O^2 = E$, and his acetic acid-residue = $C^4H^4O^2 - O^2 = C^4H^4O^2 = Ac$ [therefore = E and = Aldehyde!]; in acetic ether, therefore, $C^4H^4O^2$ would be coupled with $C^4H^4O^2$. So intimate a combination of two perfectly similar compounds is however highly improbable. Still more improbable is it that such a compound should be resolved by potash into alcohol and acetic acid, seeing that the behaviour of caustic potash with aldehyde is totally different. Even when Gerhardt admits, for this reason, that the carbon in acetic ether exists in two different forms, we are still left in doubt as to how the arrangement is to be represented.

The formation of an ether of the third class is induced, not only by the affinity which may be supposed to exist between an alcohol —HO and an acid —HO, and by that of H for O, which causes the formation of water, but moreover by the predisposing affinity of an excess of the acid for the water thus produced. The stronger this affinity of the acid, the more readily is the ether formed; hence these ethers are most easily formed by the stronger mineral acids. An organic acid, on the other hand, since its affinity for water is much less, must be used in as dry a state as possible, and repeatedly distilled with alcohol, the liquid being frequently poured back, or boiled for some time in a flask, to the neck of which is adapted an upright tube several feet long, and kept cool with wet paper, so that the vapour may be condensed and run back (*vid. Oxalic Ether*). Or, according to Gaultier de Claubry, a non-volatile acid is heated in a tubulated retort till it begins to decompose, and the alcohol then dropped upon it through the tubulure (*vid. Oxalic Ether*). But though organic acids, when merely heated with alcohol, produce compound ethers but very slowly or not at all, the formation of these compounds takes place very easily when sulphuric or hydrochloric acid is added, in consequence of the great tendency of these acids to induce the formation of water.

In ethers of the third class, the acid is completely neutralized and masked; it has lost not only its sour taste and its power of reddening litmus, but likewise all its other reactions. Thus, sulphate of methyl, C^2H^3O,SO^3, does not at first precipitate baryta-salts; but as soon as the ether begins to decompose, the reactions of the acid become apparent.

The radical-theory regards these compound ethers as salts, that is to say, as compounds of a hypothetically anhydrous acid with an organic oxide, supposed to be analogous to a metallic oxide; *e. g.*, with oxide of methyl, C^2H^3,O (formic ether), with oxide of ethyl, C^4H^5,O (common or vinic ether), or with oxide of amyl, $C^{10}H^{11},O$ (amylic ether), the acid being completely neutralized by the bases. But these so-called basic oxides exhibit in other respects no basic character whatever. They have no alkaline taste or reaction. When brought in contact with acids, they do not neutralize them and form compound ethers (with the single exception of methylic ether with anhydrous sulphuric acid), though they ought in fact to do so with greater facility than the alcohols, $C^2H^4O^2$, $C^4H^6O^2$, and $C^{10}H^{12}O^2$, which contain 1H and 1O more. Moreover, in true salts, the acids retain their peculiar reactions, whereas in the compound ethers they

do not. Aqueous solution of potash added to these compounds does not separate the so-called base (the ether) immediately, as it does when added to the compound of an acid with an earth or a metallic oxide, but slowly and often only when aided by heat; moreover, the compound thus separated is not an ether, but always an alcohol, inasmuch as the residue of the alcohol, at the moment of separation, again takes up 1H and 1O from the water, and thus the alcohol is reproduced.* When, on the contrary, an ether is dissolved in water, it remains unaltered and is not converted into an alcohol. Even perfectly dry fixed alkalis, which only act when aided by heat, do not separate a simple ether from the compound ether, but give rise to a much more complete decomposition. (*Comp.* pp. 213, 214.)

In accordance with the idea that ethers of the third class are compounds of a kind of metallic oxide with an acid, the radical-theory likewise regards the ethers of the second class (*Aſer.* p. 190) as compounds of a kind of metal with a salt-radical. Thus, $C^2H^3I = C^2H^3,I$ = iodide of methyl; $C^4H^5Br = C^4H^5,Br$ = bromide of ethyl; $C^{10}H^{11}Cl = C^{10}H^{11},Cl$ = chloride of amyl. As potassium, for example, in combination with bromine forms bromide of potassium, so ethyl combined with the same element forms bromide of ethyl; and as Potassium + O + NO^5 forms nitrate of potash, so Ethyl + O + NO^5 forms nitrate of ethyl-oxide (nitric ether). But against this it must be urged that these metalloidal compounds, C^2H^3, C^4H^5, and $C^{10}H^{11}$, are not known [*vid.* alcohol-radicals, pp. 170–174], and that whereas all metallic iodides, bromides, and chlorides precipitate a solution of silver, these ethers of the second class have no action upon it.†

From all these considerations we must suppose that the alcohol-residue in the compound ether, even if it has the same composition as the simple ether, differs from it totally in the mode of arrangement of the atoms; moreover, that the atoms of the acid or of the acid-residue attach themselves to those of the alcohol-residue in such a manner that the peculiar reactions of the acid are destroyed; but that, nevertheless, the atoms of the two substances are not completely united into a primary organic compound, inasmuch as the compound ether is again resolved by aqueous alkalis, and sometimes even by water alone, into alcohol and acid.

In many ethers of the third class, part or all of the hydrogen may be replaced by chlorine; in some, the chlorine exerts its substituting action principally on the alcohol-residue,—in a few, as in salicylic and anisic ether, on the acid-residue.

Ethers of the third class are generally watery or only liquids; a few, however, are crystalline. They volatilize without decomposition; some of them are lighter, others heavier than water; and they are highly combus-

* Is not this in strict analogy with the action of potash on nearly all metallic salts? When an alkali is added to a solution of sulphate of copper, for example, the blue precipitate formed is not the anhydrous, but the hydrated oxide; and precipitation takes place, because this hydrated oxide is insoluble in water. Now when potash is added to acetic ether (acetate of ethyl) no immediate separation takes place, because alcohol, the analogue of the hydrated metallic oxide, is easily soluble in water; and in a similar manner, pure potash does not precipitate chloride of barium, because baryta is soluble in water. But when aqueous solution of potash is added to acetate of amyl, acetate of potash is formed, and amylic alcohol separated, because this alcohol is but sparingly soluble in water. [W.]

† In some cases, however, as in the action of iodide of ethyl on potassium-alcohol (pp. 17, 201) the action of these compounds is precisely analogous to that of the metallic iodides, bromides, &c. [W.]

tible. They are sparingly soluble in water, but mix in all proportions with common alcohol and ether.—Only one of these compound ethers exhibits a slightly acid character, viz., salicylate of methyl, inasmuch as it forms a compound with potash.

Tabular View of Ethers of the Third Class.

I. Formed from Wood-spirit: *Methyl-ethers.* [Formester.]

1. *With Mineral Acids.*

$C^2H^3O,CS^2 = C^3H^3S^2O$, Sulphocarbonate of Methyl-oxide.
$C^2H^3S,CS^2 = C^3H^3S^3$, Sulphocarbonate of Methyl-sulphide.
$3C^2H^3O,BO^3 = C^6H^9BO^6$ and $C^2H^3O,2BO^3 = C^2H^3B^2O^7$ Borates of Methyl; Boracic Methyl-ethers.
$C^2H^3O,SO^3 = C^2H^3SO^4$, Sulphate of Methyl; Sulphuric Methyl-ether.
$C^2H^3O,NO^5 = C^2H^3NO^6$, Nitrate of Methyl; Nitric Methyl-ether.

2. *With Organic Acids.*

Alcohol-residue.					Acid-residue.				Compound Ether.				
C	H	Cl	O	+	C	H	Cl	O	= C	H	Cl	O	
2	3		1		2	1		3	4	4		4	Formic methyl-ether.*
2	2	1	1		2	1		3	4	3	1	4	Chlorinated methyl-ether.
2	3		1		4	3		3	6	6		4	Acetic methyl-ether.
2	1	2	1		4	3		3	6	4	2	4	Acetic methyl-ethers altered by chlorine.
2		3	1		4	3		3	6	3	3	4	
2		3	1		4		3	3	6		6	4	
2	3		1		8	7		3	10	10		4	Butyric methyl-ether.
2	3		1		10	9		3	12	12		4	Valeric methyl-ether.
2	3		1		12	11		3	14	14		4	Caproic methyl-ether.
2	3		1		14	5		3	16	8		4	Benzoic methyl-ether.
2	3		1		14	5		5	16	8		6	Salicylic methyl-ether.
2	2	1	1		14	5		5	16	7	1	6	Salicylic methyl-ethers altered by chlorine. Similarly with bromine.
2	1	2	1		14	5		5	16	6	2	6	
2	3		1		14	4	X	5	16	7	X	6	Indigotic methyl-ether.
2	3		1		16	7		5	18	10		6	Anisic methyl-ether.
2	3		1		16	6	Br	5	18	9	Br	6	Bromanisic methyl-ether.
2	3		1		16	6	X	5	18	9	X	6	Nitranisic methyl-ether.
2	3		1		16	15		3	18	18		4	Caprylic methyl-ether.
2	3		1		36	33		3	38	36		4	Elaidic methyl-ether.
4	6		2		4			6	8	6		8	Oxalic methyl-ether.
4	6		2		12	8		14	16	14		16	Mucic methyl-ether.
4	6		2		16	12		6	20	18		8	Suberic methyl-ether.
4	6		2		8	4		6	12	10		8	Succinic methyl-ethers.
6	9		3		12	5		11	18	14		14	Citric methyl-ether.

II. Formed from Alcohol: *Vinic Ethers.* [Vinester.]

1. *With Mineral Acids.*

$C^4H^5O,CS^2 = C^5H^5S^2O$, Sulphocarbonate of ethyl-oxide.
$C^4H^5S,CS^2 = C^5H^5S^3$, Sulphocarbonate of ethyl-sulphide.
$C^4H^5O,CO^2 = C^5H^5O^3$, Carbonic ether.
$C^4H^3Cl^2O,CO^2 = C^5H^3Cl^2O^3$, Chlorinated carbonic ether.
$C^5Cl^5O,CO^2 = C^5Cl^5O^3$, Perchlorinated carbonic ether.
$3C^4H^5O,BO^3 = C^{12}H^{15}BO^6$ and $C^4H^5O,2BO^3 = C^4H^5B^2O^7$. Two kinds of Boracic ether.

* Or Formiate of Methyl: it is unnecessary to give the two names in every case.

C^4H^5O,SO^2 = $C^4H^5SO^3$, Sulphurous ether.
C^4H^5O,NO^3 = $C^4H^5NO^4$, Nitrous ether.
C^4H^5O,NO^5 = $C^4H^5NO^6$, Nitric ether.
$2C^4H^5O,SiO^2$ = $C^8H^{10}SiO^4$; $C^4H^5O,SiO^2 = C^4H^5SiO^3$; and $C^4H^5O,2SiO^2 = C^4H^5Si^2O^5$. Three kinds of Silicic ether.

2. *With Organic Acids.*

Alcohol-residue.				+	Acid-residue.				=	Compound Ether.				
C	H	Cl	O		C	H	Cl	O		C	H	Cl	O	
4	5		1		2	1		3		6	6		4	Formic ether.
4	5		1		2		1	3		6	5	1	4	Modified by chlorine.
4	3	2	1		2	1		3		6	4	2	4	
4		5	1		2		1	3		6		6	4	
4	5		1		4	3		3		8	8		4	Acetic ether.
4	3	2	1		4	3		3		8	6	2	4	Modifications containing chlorine.
4	5		1		4		3	3		8	5	3	4	
4	2	3	1		4	3		3		8	5	3	4	
4	1	4	1		4	3		3		8	4	4	4	
4		5	1		4	3		3		8	3	5	4	
4		5	1		4	2	1	3		8	2	6	4	
4		5	1		4	1	2	3		8	1	7	4	
4		5	1		4		3	3		8		8	4	= $C^4Cl^4O^2$ = Chloraldehyde.
4	5		1		6	3		3		10	8		4	Acrylic ether.
4	5		1		6	5		5		10	10		6	Lactic ether.
4	5		1		8	7		3		12	12		4	Butyric ether.
4	5		1		8	5	2	3		12	10	2	4	Chlorobutyric ether.
4	5		1		10	3		5		14	8		6	Pyromucic ether.
4	5		1		10	9		3		14	14		4	Valerianic ether.
4	5		1		12	11		3		16	16		4	Caproic ether.
4	5		1		14	5		3		18	10		4	Benzoic ether.
4	5		1		14	5		5		18	10		6	Salicylic ether.
4	5		1		14	4	X	5		18	9	X	6	Indigotic ether.
4	5		1		14	13		3		18	18		4	Œnanthylic ether.
4	5		1		16	7		5		20	12		6	Anisic ether.
4	5		1		16	6	Br	5		20	11	Br	6	Bromanisic ether.
4	5		1		16	6	Cl	5		20	11	Cl	6	Chloranisic ether.
4	5		1		16	6	X	5		20	11	X	6	Nitranisic ether.
4	5		1		16	15		3		20	20		4	Caprylic ether.
4	5		1		18	7		3		22	12		4	Cinnamic ether.
4	5		1		18	6	X	3		22	11	X	4	Nitrocinnamic ether.
4	5		1		18	9		7		22	14		8	Veratric ether.
4	5		1		20	9		9		24	14		10	Opianic ether.
4	5		1		32	31		33		36	36		4	Palmitic ether.
4	5		1		34	3		3		38	38		4	Margaric ether.
4	5		1		36	33		3		40	38		4	Elaidic ether.
8	10		2		4			6		12	10		8	Oxalic ether.
8		10	2		4			6		12		10	8	Chloroxalic ether.
8	10		2		8	2		6		16	12		8	Fumaric ether.
8	10		2		8	4		6		16	14		8	Succinic ether.
8		10	2		8	1	3	6		16	1	13	6	Chlorosuccinic ether.
8	10		2		10	6		6		18	16		8	Pyromucic ether.
8	10		2		12	8		6		20	18		8	Adipic ether.
8	10		2		12	8		14		20	18		16	Mucic ether.
8	10		2		16	12		6		24	22		8	Suberic ether.
8	10		2		20	14		6		28	24		8	Camphoric ether.
8	6	4	2		20	14		6		28	20	4	8	Chlorocamphoric ether.
8	10		2		20	16		6		28	26		8	Sebacic ether.
12	15		3		12	3		9		24	18		12	Aconitic ethers.
12	15		3		12	5		11		24	20		14	Citric ether. Another variety contains 1HO more.

III. From Fusel-oil: *Amyl-ethers.* [Mylester.]

$3C^{10}H^{11}O,BO^3 = C^{30}H^{33}BO^6$, and $C^{10}H^{11}O,2BO^3 = C^{10}H^{11}B^2O^7$. Two kinds of Boracic Amyl-ether.

$2C^{10}H^{11}O,HO,PO^3 = C^{20}H^{22}PO^6$, and $C^{10}H^{11}O,2HO,PO^3 = C^{10}H^{13}PO^6$. Two kinds of Phosphorous Amyl ether.

$C^{10}H^{11}O,NO^3$	$= C^{10}H^{11}NO^4$,	Nitrous amyl-ether.
$2C^{10}H^{11}O,SiO^2$	$= C^{20}H^{22}SiO^4$,	Silicic amyl-ether.
$C^{10}H^{11}O,C^2HO^3$	$= C^{12}H^{12}O^4$,	Formic amyl-ether.
$C^{10}H^{11}O,C^4H^3O^3$	$= C^{14}H^{14}O^4$,	Acetic amyl-ether.
$C^{10}H^9Cl^2O,C^4H^3O^3$	$= C^{14}H^{12}Cl^2O^4$,	Chloracetic amyl-ether.
$C^{10}H^{11}O,C^{10}H^9O^3$	$= C^{20}H^{20}O^4$,	Valerianic amyl-ether.
$2C^{10}H^{11}O,C^4O^6$	$= C^{24}H^{22}O^8$,	Oxalic amyl-ether.

c. Amethanes. [Amester.]

These bodies must be regarded as 1 At. of a bibasic acid or 2 At. of a monobasic acid, converted by the action of ammonia and an alcohol, half into an amide, and half into a compound ether of the third class.

1 At. oxalic acid (regarded as bibasic) with 2 At. alcohol yields 4 At. water and oxalic ether:

$$C^4H^2O^8 + 2C^4H^6O^2 = 4HO + 2C^4H^5O,C^4O^6.$$

On the other hand, 1 At. oxalic acid with 2 At. ammonia, yields 4 At. water and oxamide:

$$C^4H^2O^8 + NH^3 = 4HO + C^4H^4N^2O^4.$$

But if only 1 At. alcohol acts upon 1 At. oxalic acid, the products are 2 At. water and 1 At. oxalovinic acid:

$$C^4H^2O^8 + C^4H^6O^2 = 2HO + C^4H^6O^2,C^4O^6.$$

Similarly when only 1 At. ammonia acts upon 1 At. oxalic acid, the products are 2 At. water and oxamic acid:

$$C^4H^2O^8 + NH^3 = 2HO + C^4H^3NO^6.$$

If now we suppose 1 At. oxalic acid to be acted on by 1 At. ammonia and 1 At. alcohol, 4 At. water will be separated and 1 At. of an amethane produced:

$$C^4H^2O^8 + NH^3 + C^4H^6O^2 - 4HO = C^8H^7NO^6.$$

Amethanes are most readily produced by treating an ether of the third class with small quantities of ammonia, so as to eliminate only half the alcohol; if a larger quantity of ammonia be used, the ether may be completely transformed into an amide.

Thus, 1 At. oxalic ether with 1 At. ammonia forms oxamethane and alcohol:

$$2C^4H^5O,C^4O^6 + NH^3 = C^4H^7N,C^4O^6 + C^4H^6O^2.$$

But if another atom of ammonia be added, oxamide is formed, and a second atom of alcohol is eliminated:

$$C^4H^7N,C^4O^6 + NH^3 = C^4H^4N^2O^4 + C^4H^6O^2.$$

This amethane may be regarded in various ways:—*a.* As a half amidogen- and half ether-compound of oxalic acid (or, what comes to the

same thing, if we regard oxalic acid as monobasic = C^2HO^4, as a compound of 1 At. oxamide, $C^2H^3NO^2$, with 1 At. oxalic ether, $C^6H^5O^4$).—*b.* As the vinic ether of oxamic acid (oxamate of ethyl). (Balard.)—*c.* As an amide of oxalovinic acid:

	a. C	H	N	O		*b.* C	H	N	O		*c.* C	H	N	O
Oxalic acid	4	2		8	Oxamic acid	4	3	1	6	Oxalovinic acid	8	6		8
+ Alcohol + Ammonia	4	9	1	2	+ Alcohol	4	6		2	+ Ammonia		3	1	
	8	11	1	10		8	9	1	8		8	9	1	8
− 4 Water		4		4	− 2 Water		2		2	− 2 Water		2		2
Oxamethane	8	7	1	6		8	7	1	6		8	7	1	6

d. According to Gerhardt, this compound is formed from the residues of alcohol, $C^4H^6O^2$, ammonia, NH, and oxalic acid, $C^4H^2O^4$ (p. 76).

Many other acids, inorganic as well as organic, act in a similar manner to oxalic acid, and other alcohols also like common alcohol. The amethanes formed by wood-spirit are called *Methylanes* or *Formamethanes;* those formed by common alcohol, *Ethylanes, Vinamethanes,* or simply *Amethanes;* and those formed by fusel-oil, *Amylanes,* or *Mylamethanes.* All amethanes = 1 At. of a bibasic acid (or 2 At. of a monobasic acid + 1 At. alcohol + 1 At. ammonia − 4 At. water.

If the number of elementary atoms in the compound ether and the amide of a bibasic acid be added together, and the sum divided by 2, the quotient will be the number of elementary atoms composing the amethane of the same acid.

To the class of amethanes belong the following compounds formed from wood-spirit, $C^2H^4O^2$, alcohol, $C^4H^6O^2$, and fusel-oil, $C^{10}H^{12}O^2$.

$C^2H^5NS^2O^6 = C^2H^3Ad,2SO^3 = C^2H^3O,S^2AdO^5$, Sulphomethylane.
$C^4H^5NO^4 = C^2H^3Ad,2CO^2 = C^2H^3O,C^2AdO^3$, Urethylane *or* Carbomethylane.
$C^6H^5NO^6 = C^2H^3Ad,C^4O^6 = C^2H^3O,C^4AdO^5$, Oxamethylane.
$C^6H^7NO^4 = C^4H^5Ad,2CO^2 = C^4H^5O,C^2AdO^3$, Urethane *or* Carbethylane.
$C^3H^7NO^5 = C^4H^5Ad,C^4O^6 = C^4H^5O,C^4AdO^5$, Oxamethane.
$C^6H^2Cl^5NO^5 = C^4Cl^5Ad,C^4O^6 = C^4Cl^5O,C^4AdO^5$, Chloroxamethane.
$C^{14}H^{13}NO^6 = C^{10}H^{11}Ad,C^4O^6 = C^{10}H^{11}O,C^4AdO^5$, Oxamylane.

d. Copulated Acids, Copulated Salts.

Many organic compounds, viz., nuclei in the pure state, nuclei combined with 2 At. hydrogen, alcohols, aldides, or monobasic or bibasic acids, form, with an excess of an inorganic or a stronger organic acid, acting upon them either in the anhydrous or the highly-concentrated state,—sometimes at ordinary temperatures, sometimes with the aid of heat, sometimes only in presence of a fixed alkali, and generally with elimination of water,—an intimate acid compound, a copulated acid, which unites as a whole with salifiable bases, forming peculiar salts, which are soluble in water, even if the salts of the non-copulated acid are insoluble.

The organic compound thus united with the acid is called the COPULA (*der Paarling*).

If the compound is formed by means of an anhydrous inorganic acid, no water is eliminated; but when the acting acid is an organic acid, perfectly dried *per se,* a number of atoms of water are generally separated, equal to the number of atoms of hydration-water which the radical-theory supposes to exist in the acid. The excess of the acting acid serves,

by its affinity for the water, to facilitate the separation of that compound, and to take it up.

Copulated acids may be compared to ethers of the third class, excepting that they may be formed by other compounds besides alcohols, and that they contain at least twice as much acid as the corresponding compound ethers; hence in these compounds the characteristic properties of the generating acid are not completely masked.

In these compounds, the following law established by Gerhardt holds good (*Comp. rend.* 20, 1648). The saturating power of a copulated compound is less by unity than the sum of the saturating powers (p. 206) of the two substances of which it is formed. Or, 1 At. of the copulated acid saturates 1 At. less of base than the two generating substances would have saturated if they had acted separately. The compound ether, which 1 At. of an alcohol forms with 1 At. of a monobasic acid, is, therefore, a neutral compound; for $0+1-1=0$; similarly, 2 At. alcohol with 1 At. of a bibasic acid,—in which case we must consider that, first, 1 At. alcohol enters, and then a second atom : $0+2-1=1$; then, $0+1-1=0$. But when 1 At. of a neutral compound unites with 1 At. of a bibasic acid, we have, $0+2-1=1$; that is to say, the resulting copulated acid has a saturating power=1. Similarly, a copulated acid formed from a neutral substance and 1 At. of a terbasic acid, such as phosphoric acid, has a basic power=2; for $0+3-1=2$. Further, when a monobasic organic acid is united with 2 At. of a monobasic acid, the copulated acid is bibasic; *e. g.*, sulphobenzoic acid, $1+2-1=2$; and the copulated acid from a bibasic acid and 2 At. of a monobasic acid is terbasic; *e. g.*, Sulphosuccinic acid, $2+2-1=3$.

This law holds good throughout, with the exception of a very few cases to be afterwards mentioned, which perhaps admit of special explanation. It is further to be observed; that all organic acids which form copulated acids, are (with very few exceptions, *vid. inf.*) bibasic. This circumstance is certainly in favour of Gerhardt's view, that those inorganic acids which form copulated acids, are likewise bibasic, and should therefore have twice the atomic weights usually assigned to them, viz., CS^2; CO^2; SO^2; and SO^3 (pp. 201, 201); but in this instance also an exception is presented by nitroglycolic acid. (*Comp.* also Mitscherlich, *J. pr. Chem.* 22, 198; Berzelius, *Jahresber.* 21, 105.)

On the constitution of the copulated acids the following views may be proposed :

a. They are compounds of organic bodies of a comparatively indifferent character with anhydrous mineral acids, or with hypothetically anhydrous organic acids. Thus, sulphobenzinic acid $=C^{12}H^6,2SO^3$; sulphomethylic acid $=C^2H^4O^2,2SO^3$; sulphovinic acid $=C^4H^6O^2,2SO^3$; oxalovinic acid $=C^4H^6O^2,C^4O^6$. In the formation of a metallic salt, 1, 2, or 3 At. hydrogen in the copula are replaced by 1, 2, or 3 At. of a metal; *e. g.*, sulphobenzinate of potash $=C^{12}H^5K,2SO^3$; sulphovinate of potash $=C^4H^5KO^2,2SO^3$; oxalovinate of potash $=C^4H^5KO^2,C^4O^6$.

To this view, which, even if it be not correct, may at all events be satisfactorily followed out, Gerhardt has lately given the preference, excepting that he makes no separation in the formula between the copula and the acid; thus sulphovinic acid, $C^4H^6O^2,2SO^3$, he expresses by $C^4H^6S^2O^8$ (or, according to his own equivalents, by $C^2H^6SO^4$).

b. They contain the indifferent organic bodies from which they have

been formed, *minus* 1HO; also 1 At. of water actually formed, and 2 At. of a monobasic, or 1 At. of a bibasic acid; if the acid is terbasic, like phosphoric acid, an additional atom of water is also present. Thus, sulphovinic acid would be $HO,SO^3+C^4H^5O,SO^3$; sulphomethylic acid $HO,SO^3+C^2H^3O,SO^3$; and phosphovinic acid, $2HO,C^4H^5O,PO^5$. The metallic salts of this acid are produced by the replacement of 1 or 2 HO by 1 or 2 MO. If the copulated acid contains an organic acid, the latter is supposed to exist in it, half in the hypothetically anhydrous state, and half with the quantity of the elements of water which it retains when dried *per se*. Thus, oxalovinic acid (supposing oxalic acid to be monobasic)$=HO,C^2O^3+C^4H^5O,C^2O^3$.

According to this view, which accords with the radical-theory, the copulated acids may be regarded as double salts, in which part of the acid is saturated by the copula, and the rest by water, or by a true salifiable base. This mode of representation also makes more evident the relation of the copulated acids to compound ethers of the third class. Thus, sulphate of methyl$=C^2H^3O,SO^3$, is converted into sulphomethylic acid, C^2H^3O,SO^3+HO,SO^3 by the mere addition of HO,SO^3.—¶ The formulæ of the copulated acids lately given by Williamson (*Chem. Soc. Qu. J.* IV., 235), *e. g.*, sulphovinic acid $=\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}SO^4$; sulphovinate of potash $=\left.\begin{matrix}C^2H^5\\K\end{matrix}\right\}SO^4$; are likewise in accordance with this view. ¶

If, however, the organic substance from which the copula is formed, contains no oxygen, which is the case with benzin$=C^{12}H^6$, and, therefore, cannot yield HO, we must suppose that it gives up only hydrogen, and that the oxygen is supplied from the acid, whose nature is thereby changed. Thus, sulphobenzinic acid, $HO,C^{12}H^5,S^2O^5$, must be regarded as a compound of water and $C^{12}H^5$, a body not known in the separate state, with 1 At. hyposulphuric acid. But since hyposulphuric acid, S^2O^5, is monobasic, the supposition that 2 At. of base, viz., 1HO or MO, and 1 At. of the copula should be united with 1 At. of the acid, is not in accordance with the preceding.

c. In the copulated acids of sulphuric acid, we may likewise suppose that 1 At. hydrogen is replaced by 1 At. of sulphurous acid. According to this view, sulphobenzinic acid$=HO,C^{12}H^5(SO^2),SO^3$, and sulphovinic acid$=HO,C^4H^5(SO^2)O^2,SO^3$. This was Gerhardt's earlier view (*Ann. Chim. Phys.* 72, 184), and Mitscherlich also expresses himself in its favour (*Ann. Chim. Phys.* 4, 67; 7, 6). But although this view is likewise supported by the fact, that many copulated acids cannot be formed without the aid of heat, probably because the conversion of sulphuric into sulphurous acid takes place only at high temperatures, and that several copulated acids, containing sulphuric acid, when fused with excess of hydrate of potash, yield sulphite of potash as well as sulphate; it, nevertheless, cannot include more than a small number of the copulated acids: for, in the case of carbonic acid, sulphurous acid, and the organic acids, it can only be maintained by means of hypotheses not corroborated by any other consideration; and to phosphorous and phosphoric acid it is altogether inapplicable, unless we express the latter by P^2O^5 instead of PO^5, because it is impossible that one part of an atom of P should enter the copula, while the rest remains without in the form of the acid. Moreover, two bases (the copula and water, or a metallic oxide) would be united with 1 At. of a monobasic acid.

Tabular view of the best known Copulated Acids.

I. Produced by Mineral Acids.

1. *By Bisulphide of Carbon with Wood-spirit, Alcohol, Fusel-oil, and Ethal.*

According to *a*.		According to *b*.		
Acid.	Metallic salt.	Acid.	Metallic salt.	
$C^2H^4O^2,2CS^2$	$C^2H^3MO^2,2CS^2$	$HO,C^2H^3O,2CS^2$	$MO,C^2H^3O,2CS^2$	.... (1)
$C^4H^6O^2,2CS^2$	$C^4H^5MO^2,2CS^2$	$HO,C^4H^5O,2CS^2$	$MO,C^4H^5O,3CS^2$	.... (2)
$C^{10}H^{12}O^2,2CS^2$	$C^{10}H^{11}MO^2,2CS^2$	$HO,C^{10}H^{11}O,2CS^2$	$MO,C^{10}H^{11}O,2CS^2$	.... (3)
$C^{32}H^{34}O^2,2CS^2$	$C^{32}H^{33}MO^2,2CS^2$	$HO,C^{32}H^{33}O,2CS^2$	$MO,C^{32}H^{33}O,2CS^2$	.... (4)

(1) Xanthomethylic acid.—(2) Xanthovinic acid.—(3) Xanthamylic acid.—(4) Xanthethalic acid.

2. *By Carbonic acid with Wood-spirit and Alcohol.*

According to *a*.		According to *b*.		
Acid.	Metallic salt.	Acid.	Metallic salt.	
$C^2H^4O^2,2CO^2$	$C^2H^3MO^2,2CO^2$	$HO,C^2H^3O,2CO^2$	$MO,C^2H^3O,2CO^2$	.... (1)
$C^4H^6O^2,2CO^2$	$C^4H^5MO^2,2CO^2$	$HO,C^4H^5O,2CO^2$	$MO,C^4H^5O,2CO^2$	.... (2)

(1) Carbomethylic acid.—(2) Carbovinic acid.

3. *By Phosphorous acid with Alcohol and Fusel-oil.*

According to *a*.		According to *b*.		
Acid.	Metallic salt.	Acid.	Metallic salt.	
$C^4H^6O^2,HO,PO^3$	$C^4H^5MO^2,HO,PO^3$	HO,C^4H^5O,HO,PO^3	MO,C^4H^5O,HO,PO^3	(1)
$C^{10}H^{12}O^2,HO,PO^3$	$C^{10}H^{11}MO^2,HO,PO^3$	$HO,C^{10}H^{11}O,HO,PO^3$	$MO,C^{10}H^{11}O,HO,PO^3$	(2)

(1) Vinophosphorous acid.—(2) Amylophosphorous acid.

4. *By Phosphoric acid with Alcohol and Glycerin.*

According to *a*.		According to *b*.		
Acid.	Metallic salt.	Acid.	Metallic salt.	
$C^4H^6O^2,HO,PO^5$	$C^4H^4M^2O^2HO,PO^5$	$2HO,C^4H^5O,PO$	$2MO,C^4H^5O,PO^5$	.... (1)
$C^6H^8O^6,HO,PO^5$	$C^6H^6M^2O^2,HO,PO^5$	$2HO,C^6H^7O^5,PO^5$	$2MO,C^6H^7O^5,PO^5$	.... (2)

(1) Phosphovinic acid.—(2) Phosphoglyceric acid.

5. *By Sulphurous acid with Wood-spirit in the pure state, and modified by Chlorine.*

According to *a*.		According to *b*.		
Acid.	Metallic salt.	Acid.	Metallic salt.	
$C^2H^4O^2,2SO^2$	$C^2H^3MO^2,2SO^2$	$HO,C^2H^3O,2SO^2$	$MO,C^2H^3O,2SO^2$	.... (1)
$C^2H^3ClO^2,2SO^2$	$C^2H^2ClMO^2,2SO^2$	$HO,C^2H^2ClO,2SO^2$	$MO,C^2H^2ClO,2SO^2$	.... (2)
$C^2H^2Cl^2O^2,2SO^2$	$C^2HCl^2MO^2,2SO^2$	$HO,C^2HCl^2O,2SO^2$	$MO,C^2HCl^2O,2SO^2$	.... (3)
$C^2HCl^3O^2,2SO^2$	$C^2Cl^3MO,2SO^2$	$HO,C^2Cl^3O,2SO^2$	$MO,C^2Cl^3O,2SO^2$	.... (4)

(1) Methylosulphurous acid.—(2) Chloromethylosulphurous acid.—(3) Bichloromethylosulphurous acid.—(4) Trichloromethylosulphurous acid.

Bisulphide of carbon, CS^2, is a sulphur-acid, strictly analogous to carbonic acid, CO^2, and forms copulated acids precisely corresponding to

those of the latter. The four last-named copulated sulphurous acids are the acids discovered by Kolbe (*comp.* II., 340, 341); they are regarded by Laurent and Gerhardt as compounds of 2 At. sulphuric acid with marsh-gas, C^2H^4, and its chlorine compounds, C^2H^3Cl; $C^2H^2Cl^2$; and C^2HCl^3.

Sulphuric acid forms the greatest number of copulated acids. If the copulæ are hydrocarbons or volatile acids, it is necessary to bring fuming oil of vitriol, or the cold vapour of anhydrous sulphuric acid, in contact with them; for the formation of other copulated sulphuric acids, common oil of vitriol is better adapted. In some cases a gentle heat is required to sustain the action. If the acid liquid be then diluted with water, saturated with baryta, lime, or oxide of lead, and filtered, the insoluble salt which the unaltered portion of the sulphuric acid forms with these bases, remains on the filter, and the salt of the copulated acid is found dissolved in the filtrate.

In the following table of the copulated sulphuric acids, those which contain a hydrocarbon for their copula, are placed first; then follow the acids which contain an oxygenated but not acid copula. All these copulated acids are monobasic, if they contain 1 At. of the copula to 2 At. sulphuric acid (0+2−1=1), but bibasic if the quantity of sulphuric acid amounts to 4 atoms (0+2−1=1; then 1+2−1=2). Then follow the acids containing 1 At. of a monobasic organic acid to 2 At. sulphuric acid, which are all bibasic (1+2−1=2). Lastly, sulphosuccinic acid contains 1 At. of bi-atomic succinic acid with 2 At. sulphuric acid, and should, therefore, according to Gerhardt's law, be terbasic (2+2−1=3); and so it actually is in most of its salts, but in the lead-salt it is quadrobasic=$C^8H^2Pb^4O^8,2SO^3$.

The following copulæ, united with 2 At. sulphuric acid, yield the following copulated acids:

(1)	$C^{12}H^6$	Benzin	.....	Sulphobenzinic acid.
(2)	$C^{14}H^8$	Benzoene *or* Toluol	.....	Sulphotoluic acid.
(3)	$C^{18}H^{12}$	Cumene	.....	Sulphocuminic acid.
(4)	$C^{20}H^8$	Naphthalin	.....	Sulphonaphthalic acid.
(5)	$C^{20}H^{14}$	Cymene	.....	Sulphocymenic acid.
(6)	$C^{20}H^{12}O^2$	Anethol	.....	Sulphanethic acid.
(7)	$C^{16}H^5NO^2$	Indigo-blue	.....	Sulphindigotic acid.
(8)	$C^{16}H^5NO^4$	Isatin	.....	Sulphisatinic acid.
(9)	$C^{12}H^6O^2$	Phenous acid	.....	Sulphophenilic acid.
(10)	$C^6H^8O^6$	Glycerin	.....	Sulphoglyceric acid.
(11)	$C^2H^4O^2$	Wood-spirit	.....	Sulphomethylic acid.
(12)	$C^4H^6O^2$	Alcohol	.....	Sulphovinic acid.
(13)	$C^{10}H^{12}O^2$	Fusel-oil	.....	Sulphamylic acid.
(14)	$C^{32}H^{34}O^2$	Ethal	.....	Sulphethalic acid.
(15)	$C^4H^4O^4$	Acetic acid	.....	Sulphacetic acid.
(16)	$C^{14}H^6O^4$	Benzoic acid	.....	Sulphobenzoic acid.
(17)	$C^{18}H^8O^4$	Cinnamic acid	.....	Sulphocinnamic acid.
(18)	$C^8H^6O^8$	Succinic acid	.....	Sulphosuccinic acid.

The formulæ of these copulated acids and their salts are as follows:

		According to *a*.	
	Acid.		Metallic salt.
(1)	$C^{12}H^6,2SO^3$	.....	$C^{12}H^5M,2SO^3$
(2)	$C^{14}H^8,2SO^3$	.....	$C^{14}H^7M,2SO^3$
(3)	$C^{18}H^{12},2SO^3$	.....	$C^{18}H^{11}M,2SO^3$
(4)	$C^{20}H^8,2SO^3$	.....	$C^{20}H^7M,2SO^3$
(5)	$C^{20}H^{14},2SO^3$	.....	$C^{20}H^{13}M,2SO^3$
(6)	$C^{20}H^{12}O^2,2SO^3$	.....	$C^{20}H^{11}MO^2,2SO^3$

	Acid.		Metallic salt.
(7)	$C^{16}H^{5}NO^{2},2SO^{3}$	.....	$C^{16}H^{4}MNO^{2},2SO^{3}$
(8)	$C^{16}H^{5}NO^{4},2SO^{3}$	.....	$C^{16}H^{4}MNO^{4},2SO^{3}$
(9)	$C^{12}H^{6}O^{2},2SO^{3}$	.....	$C^{12}H^{5}MO^{2},2SO^{3}$
(10)	$C^{6}H^{8}O^{4},2SO^{3}$	.....	$C^{6}H^{7}MO^{6},2SO^{3}$
(11)	$C^{2}H^{4}O^{2},2SO^{3}$	.....	$C^{2}H^{3}MO^{2},2SO^{3}$
(12)	$C^{4}H^{6}O^{2},2SO^{3}$	.....	$C^{4}H^{5}MO^{2},2SO^{3}$
(13)	$C^{10}H^{12}O^{2},2SO^{3}$	.....	$C^{10}H^{11}MO^{2},2SO^{3}$
(14)	$C^{32}H^{24}O^{2},2SO^{3}$	.....	$C^{32}H^{23}MO^{2},2SO^{3}$
(15)	$C^{4}H^{4}O^{4},2SO^{3}$	.....	$C^{4}H^{2}M^{2}O^{4},2SO^{3}$
(16)	$C^{14}H^{6}O^{4},2SO^{3}$	.....	$C^{14}H^{4}M^{2}O^{4},2SO^{3}$
(17)	$C^{18}H^{8}O^{4},2SO^{3}$	.....	$C^{18}H^{6}M^{2}O^{4},2SO^{3}$
(18)	$C^{6}H^{6}O^{6},2SO^{3}$	.....	$C^{6}H^{3}M^{3}O^{6},2SO^{3}$

According to *b*.

	Acid.		Metallic salt.
(1)	$HO,C^{12}H^{5},S^{2}O^{5}$	.....	$MO,C^{12}H^{5},S^{2}O^{5}$
(2)	$HO,C^{14}H^{7},S^{2}O^{5}$	.....	$MO,C^{14}H^{7},S^{2}O$
(3)	$HO,C^{18}H^{17},S^{2}O^{5}$	.....	$MO,C^{18}H^{17},S^{2}O^{5}$
(4)	$HO,C^{20}H^{7},S^{2}O^{5}$	.....	$MO,C^{20}H^{7},S^{2}O^{5}$
(5)	$HO,C^{20}H^{13},S^{2}O^{5}$	.....	$MO,C^{20}H^{13},S^{2}O^{5}$
(6)	$HO,SO^{3}+C^{20}H^{11}O,SO^{3}$	.....	$MO,SO^{3}+C^{20}H^{11}O,SO^{3}$
(7)	$HO,SO^{3}+C^{16}H^{4}NO,SO^{3}$	.....	$MO,SO^{3}+C^{16}H^{4}NO,SO^{3}$
(8)	$HO,SO^{3}+C^{16}H^{4}NO^{3},SO^{3}$	.....	$MO,SO^{3}+C^{16}H^{4}NO^{3},SO^{3}$
(9)	$HO,SO^{3}+C^{12}H^{5}O,SO^{3}$	.....	$MO,SO^{3}+C^{12}H^{5}O,SO^{3}$
(10)	$HO,SO^{3}+C^{6}H^{7}O^{6},SO^{3}$	.....	$MO,SO^{3}+C^{6}H^{7}O^{6},SO^{3}$
(11)	$HO,SO^{3}+C^{2}H^{3}O,SO^{3}$	.....	$MO,SO^{3}+C^{2}H^{3}O,SO^{3}$
(12)	$HO,SO^{3}+C^{4}H^{5}O,SO^{3}$	.....	$MO,SO^{3}+C^{4}H^{5}O,SO^{3}$
(13)	$HO,SO^{3}+C^{10}H^{11}O,SO^{3}$	.....	$MO,SO^{3}+C^{10}H^{11}O,SO^{3}$
(14)	$HO,SO^{3}+C^{32}H^{23}O,SO^{3}$	.....	$MO,SO^{3}+C^{32}H^{23}O,SO^{3}$
(15)	$2(HO,SO^{3})+C^{4}H^{2}O^{2}$	.....	$2(MO,SO^{3})+C^{4}H^{2}O^{2}$*
(16)	$2(HO,SO^{3})+C^{14}H^{4}O^{2}$	.....	$2(MO,SO^{3})+C^{14}H^{4}O^{2}$
(17)	$2(HO,SO^{3})+C^{18}H^{6}O^{2}$	.....	$2(MO,SO^{3})+C^{18}H^{6}O^{2}$
(18)	$3HO,C^{6}H^{3}O^{5},2SO^{3}$	.....	$3MO,C^{6}H^{3}O^{5},2SO^{3}$

Nitric acid forms copulated acids only with glycocol and leucin.

Glycocol: $C^{4}H^{5}NO^{4}$; Nitroglycolic acid: $C^{4}H^{5}NO^{4},NO^{5}$; its salts: $C^{4}H^{5}NMO^{4},NO^{5}$.

Leucin: $C^{12}H^{13}NO^{4}$; Nitroleucic acid: $C^{12}H^{13}NO^{4},NO^{5}$; its salts: $C^{12}H^{12}MNO^{4},NO^{5}$.

Hence it appears that these two acids do not accord with Gerhardt's laws, viz. (1) That true monobasic acids, like nitric acid, do not form copulated acids; and (2) That 1 At. of a neutral body united with 1 At. of a monobasic acid must form a neutral compound $(0+1-1=0)$.

The compounds of 1 At. glycocol with 1 At. sulphuric, hydrochloric, and benzoic acid are likewise monobasic copulated acids. The salts of these peculiar copulated acids may be compared with nitrates or other inorganic salts, which have taken up one or more atoms of urea from a solution containing that substance.

II. Copulated Organic Acids.

Scarcely any organic acids form copulated acids, excepting those which may in all probability be regarded as bibasic. The only exceptions to this law are the combination of glycocol with benzoic acid in hippuric acid, and that of acetic acid with bitter almond oil in mandelic acid. In most

* Berzelius (*Jahresber.* 23, 321) prefers the halved formulæ $HO,SO^{3}+C^{2}HO$ and $MO,SO^{3}+C^{2}HO$.

of these compounds, the organic acid must be supposed to exist in the hypothetically anhydrous state.

With *Oxalic acid.*

According to *a*.

Acid.		Metallic salt.		
$C^4H^6O^2,C^4O^6$	.....	$C^4H^5MO^2,C^4O^6$	.....	(1)
$C^4HCl^5O^2,C^4O^6$	.....	$C^4Cl^5MO^2,C^4O^6$	.....	(2)
$C^{10}H^{12}O^2,C^4O^6$	.....	$C^{10}H^{11}MO^2,C^4O^6$	.....	(3)

According to *b*.

Acid.		Metallic acid.		
$HO,C^2O^3 + C^4H^5O,C^2O^3$	....	$MO,C^2O^3 + C^4H^5O,C^2O^3$	.....	(1)
$HO,C^2O^3 + C^4Cl^5O,C^2O^3$	....	$MO,C^2O^3 + C^4Cl^5O,C^2O^3$	.....	(2)
$HO,C^2O^3 + C^{10}H^{11}O,C^2O^3$	....	$MO,C^2O^3 + C^{10}H^{11}O,C^2O^3$	.....	(3)

(1) Oxalovinic acid.—(2) Chloroxalovinic acid.—(3) Oxalamylic acid.

With *Tartaric* and *Racemic* acid (which are isomeric).

According to *a*.

Acid.		Metallic salt.		
$C^2H^4O^2,C^8H^4O^{10}$	.....	$C^2H^3MO^2,C^8H^4O^{10}$	.....	Tartromethylic acid.
$C^4H^6O^2,C^8H^4O^{10}$	.....	$C^4H^5MO^2,C^8H^4O^{10}$	.....	Tartrovinic and tartro-racemic acid.
$C^{10}H^{12}O^2,C^8H^4O^{10}$	.....	$C^{10}H^{11}MO^2,C^8H^4O^{10}$	.....	Tartramylic acid.

According to *b*.

Acid.		
$HO,C^4H^3O^5 + C^2H^3O,C^4H^2O^5$	.....	Tartromethylic acid.
$HO,C^4H^2O^5 + C^4H^5O,C^4H^2O^5$	.....	Tartrovinic and Racemovinic acid.
$HO,C^4H^2O^5 + C^{10}H^{11}O,C^4H^2O^5$	.....	Tartramylic acid.

With *Mucic* and *Camphoric acid.*

According to *a*.

Acid.		Metallic Salt.		
$C^4H^6O^2,C^{12}H^8O^{14}$	.....	$C^4H^5MO^2,C^{12}H^8O^{14}$	.....	Mucovinic acid.
$C^4H^6O^2,C^{20}H^{14}O^6$	.....	$C^4H^5MO^2,C^{20}H^{14}O^6$	.....	Camphovinic acid.

According to *b*.

Acid.		
$HO,C^8H^4O^7 + C^4H^5O,C^8H^4O^7$	.....	Mucovinic acid.
$HO,C^{10}H^7O^3 + C^4H^5O,C^{10}H^7O^3$	.....	Camphovinic acid.

Formic acid, $C^2H^2O^4$, united with bitter almond oil, $C^{14}H^6O^2$, forms mandelic acid, $C^{14}H^6O^2,C^2H^2O^4$, whose metallic salts$=C^{14}H^5MO^2,C^2H^2O^4$. It presents three points of exception,—inasmuch as it is monobasic,—forms a monobasic acid by combining in equal numbers of atoms with a neutral compound,—and the combination takes place without elimination of water.

c. Saponifiable Fats, yielding Glycerin.

GLYCERIDES.

SCHEELE. *Opuscula,* 1, 125; 2, 175.
J. D. BRANDIS. *Comm. de oleor. unguinos. natura.* Gött. 1788.
A. VOGEL. *Ann. Chim.* 58, 154.

FREMY. Saponification. *Ann. Chim.* 63, 25.—Action of Sulphuric acid. *Ann. Chim. Phys.* 65, 113; also *J. pr. Chem.* 12, 384.

CHEVREUL. *Ann. Chim.* 88, 225; also *Schw.* 14, 420; also *A. Tr.* 24, 1, 237.—*Ann. Chim.* 94, 80; also *A. Tr.* 25, 2, 256.—*Ann. Chim.* 94, 113; also *N. Tr.* 2, 2, 212.—*Ann. Chim.* 94, 225.—*Ann. Chim. Phys.* 2, 329.—*Ann. Chim. Phys.* 13, 337; abstr. *N. Tr.* 6, 1, 252.—*Ann. Chim. Phys.* 22, 27 and 366.

——— *Recherches sur les corps gras d'origine animale.* Paris, 1823.

BRACONNOT. *Ann. Chim.* 93, 225; also *A. Tr.* 25, 2, 307.

SAUSSURE.—Analysis of Fats. *Ann. Chim. Phys.* 13, 338; also *Schw.* 28, 389; also *N. Tr.* 5, 2, 112.

BOUDET.—Action of Hyponitric Acid on Oils. *Ann. Chim. Phys.* 50, 390; also *J. Chim. méd.* 8, 641.

LECANU. *Ann. Chim. Phys.* 55, 192.

PELOUZE & BOUDET. *Ann. Chim. Phys.* 69, 43; also *J. Chim. méd.* 24, 385; also *J. pr. Chem.* 15, 287.

GUSSEROW. *Kastn. Arch.* 19, 69 and 219.

SCHNEIDER.—Oxidation of the volatile Distillation-products of Fats. *Ann. Ch. Pharm.* 70, 107; abstr. *Jahresber. L. & K.* 1849, 344; *Chem. Gaz.* 1849, 334.

SCHAARLING.—Action of superheated steam on Fats. *J. pr. Chem.* 50, 375; abstr. *Jahresber. L. & K.* 1849, 406.

ARZBÄCHER.—Behaviour of Fixed Oils with Bichromate of Potash and Sulphuric Acid. *Ann. Pharm.* 73, 199; abstr. *Jahresber. L. & K.* 1850, 406.

DUFFY.—On certain Isomeric transformations of Fats. *Chem. Soc. Qu. J.* 5, 197.

History. The term *Fat* was originally applied to all compounds consisting of carbon, hydrogen, and a small quantity of oxygen, which either at ordinary temperatures form viscid, oily liquids, greasy and leaving a permanent stain on paper, or are converted into such liquids by heat,—which require a strong heat to make them boil, and then distil over in a state of complete, or nearly complete decomposition,—burn with a bright flame, depositing little or no soot,—and are insoluble in water, but soluble in alcohol and in ether. The Romans appear to have been acquainted with the preparation of soap from many of these fats by treating them with aqueous alkalis, having derived their knowledge from the Germans or from the Gauls.

Fats were divided, according to their various degrees of fusibility, into *Liquid Fats* or *Fatty Oils, Expressed Oils*, or *Fixed Oils*, which, according as they dry up or remain greasy when exposed to the air in thin layers, were subdivided into *Drying Oils* and *Non-drying Oils*,—and into *Solid Fats*, such as lard, tallow, wax, spermaceti, cholesterin, &c.

Chevreul, to whose fundamental investigations we are indebted for the greater part of our knowledge of this subject, showed, nearly at the same time with Braconnot, that fats, as they occur in nature, are for the most part, mixtures or combinations of different simple fats, *e. g.*, of olein, stearin, and margarin, in variable proportions, the consistence and fusibility of the mixture varying accordingly. He showed, moreover, that certain fats (non-saponifiable fats), neither dissolve nor undergo any other change when boiled with aqueous alkalis, whereas most of these bodies form soaps with aqueous alkalis and with certain heavy metallic oxides; that, in this process of saponification, the fats do not combine in their

original state with the alkalis, but that—as already rendered probable by the experiments of Scheele (*Opuscula*, 1, 125; 2, 175-177) and of Fremy (*Ann. Chim.* 63, 28)—they are thereby resolved into two products, viz., first, a fatty acid, which combines with the alkali and forms the soap, and differs in its composition according to the nature of the fat,—and secondly, in most cases, the substance called *Glycerin*, which Scheele obtained by treating fixed oils with lead-oxide and water. He showed that the sum of the weights of these two products, in their utmost state of dryness, exceeds that of the fat employed, and consequently that hydrogen and oxygen from the water must likewise contribute, in equal numbers of atoms, to the formation of the product; whence he concluded that these saponifiable fats are not primary organic compounds, but substances analogous to the ethers of the third class, viz., compounds of various fatty acids with glycerin, *minus* a certain quantity of HO, just as ethers of the third class are compounds of alcohol with oxygen acids *minus* a certain quantity of HO.

The *Ferussac. Bullet. des sc. math. phys. et chim.* 1828, July, 85, contains the following remarks by Saigey: "*La théorie des corps gras établie par M. Chevreul fut d'abord très peu goutée en Allemagne, en Angleterre, et en Italie. M. Gmelin l'attaque particulièrement, et malgrè les nouvelles et nombreuses recherches auxquelles s'adonne leur inventeur, nonobstant l'accueil favorable des chimistes françois, il est probable que cette théorie eût fini par être entièrement abandonnée, si la découverte de Serturner ne fût venue lui servir d'appui.*" Whoever has observed the manner in which, from the publication of the second edition of this *Handbuch* (1822), I have acknowledged the truth and value of Chevreul's theories and experiments, and have perhaps explained and described them more fully than has been done in any French work, will certainly ask with astonishment, what can have led M. Saigey to indulge in the vapid declamation just quoted.

In accordance with the investigations of Chevreul, which have since been confirmed and extended, the family of the fats has been broken up, and its members arranged according to their chemical nature, as follows:

1. *Unsaponifiable Fats.* These substances remain perfectly unaltered even after long boiling with aqueous potash. According to their composition, they belong partly to the hydrocarbons, such as Paraffin, partly to the aldides, as perhaps Succin and Cholesterin, partly to the alcohols, as Ethal.

2. *Fatty acids* or *Soap-acids.* Obtained chiefly by the saponification of saponifiable fats. They combine with salifiable bases, without any further addition, and are completely separated therefrom in their original state by stronger acids; hence they properly belong to the class of organic acids, and are in fact included therein. According to their boiling points, they may be divided into *Volatile Fatty acids*, as Butyric, Capric acid, &c.; and *Fixed Fatty acids*, as Stearic, Margaric, Oleic acid, &c.

3. *Saponifiable Fats.* These fats do not combine in their entire state with alkalis; but in contact with alkalis and with water are gradually resolved into a fatty acid which unites with the base, and forms a soapy salt, and a neutral body, which, in most fats of this kind, is glycerin, but in some, as cerin and spermaceti, is a non-saponifiable fat. Since the behaviour of these last-mentioned fats in saponification has not yet been completely made out, their consideration must be deferred to the special part of this work.

In this place we shall treat generally of those saponifiable fats which, by saponification, are resolved into a fatty acid and glycerin, and may therefore be distinguished by the term *Glycerides.*

Sources of Glycerides. 1. In the vegetable kingdom: As oil and tallow, especially in the seeds of a great number of plants, and most frequently in the *testa*,—rarely in the *albumen* (poppy), the *radicle*, and the fleshy matter surrounding the seed (olive). Rarely in the root (*Cyperus esculentus*). (Wahlenberg, *N. Gehl.* 8, 113).—2. In the animal kingdom: As oil, suet and lard, mostly enclosed in the cellular tissues, and in particular cavities of the body.

Formation. It is perhaps possible to produce glycerides artificially by the union of a fatty acid and glycerin, by treating a mixture of those substances with bodies having a strong attraction for water; such an attempt has in fact been made by Pelouze & Gélis, and by Gerhardt with the fat of butter (*q. v.*). All other statements about the artificial formation of fats appear to be destitute of foundation. The following are some of these supposed modes of formation: 1. A yellow fat is said to have been formed by the action of nitric acid on muscular flesh. It is most probable, however, that the fat existed ready formed in the flesh, and was merely altered by the nitric acid. Chevreul (*Recherches*, 201) did not obtain any fat by treating pure fibrin with nitric acid.—According to Berzelius, boiling alcohol or ether extracts an offensive tallowy substances from albumen, fibrin, blood-red and casein.—This fat was already present in the above-named animal substances. Chevreul (*Analyse organique*, 84) obtained the same quantity of stearic, margaric, and oleic acid from elephants' tendons, whether he first boiled the tendons in alcohol, and saponified the fat thus obtained with potash, or boiled the tendons in their original state with potash. The fibrin of ox-blood yielded to alcohol and ether the same quantity of fat that Chevreul obtained from it by the action of nitric acid.—3. Brandes (*N. Tr.* 3, 1, 377) by repeatedly distilling alcohol over oil of vitriol, and rectifying the final distillate, which had a strong sulphurous smell, over lime and potash, obtained in the receiver an oil which sank to the bottom of the liquid.—Was this modified fusel-oil?

Preparation. The fat is separated by pressure from the vegetable or animal tissue, at the ordinary temperature, if it be sufficiently fluid, otherwise at a higher temperature; sometimes, however, the fat separates spontaneously by simple fusion.—2. The fat is dissolved out by boiling alcohol or ether, whereupon it separates, sometimes on cooling, sometimes on evaporation or on being mixed with water,—and is afterwards washed with water.—But the fat obtained by either of these methods is, generally, a mixture of several simple fats, which may be separated, in some cases, in consequence of their different degrees of fusibility, by pressing them at a temperature at which one is solid and the other liquid, sometimes, from their different degrees of solubility in alcohol and ether, by treating them with these liquids.

Properties. In the solid state, the fats are white, transparent, or translucent. Some of them are crystalline, others have a close, splintery fracture. Specific gravity, between 0·892 and 0·930. At a certain degree of cold, they are brittle and friable; at a less degree, more or less soft. Melting points ranging from 20 degrees and more below 0° to +61°.

To determine accurately the melting point of a fat, a thin glass tube is drawn out to a fine capillary termination; the melted fat sucked into it; the tube placed, together with a thermometer, in water; and the water

gradually heated, till the appearance of transparency in the capillary tube shows that the fat is melted; if the water be then left to cool, it will after a while become opaque, and thus indicate the solidifying point, which generally lies 1 or 2 degrees below the melting point. (Redtenbacher, *Ann. Pharm.* 35, 46.) Bunsen (*Ann. Pharm.* 37, 25) seals the capillary tube at both ends before immersing it in the water.—Heintz (*Ann. Pharm.* 60, 58) plunges a small-bulbed thermometer into the mass heated 10° or 20° above its melting point; draws it out; holds it against a window or a lamp, in such a manner that a distinct image of the light may be formed upon the bulb; and reads off the temperature at the moment when the image becomes dull.—¶ Duffy (*Chem. Soc. Qu. J.* V., 200) places a small portion of the fat in a loop formed at the end of a piece of platinum wire; suspends the wire, together with a thermometer, in water; raises the temperature gradually, and reads it off at the moment when the bead becomes transparent. ¶

Fats in the melted state form colourless (or occasionally yellowish or greenish) viscid oils, greasy to the touch, and making a permanent stain on paper. They are not volatile without decomposition. Only in vacuo may certain fats be almost wholly distilled without decomposition. (Chevreul.) Fats are neutral to vegetable colours. They are inodorous, and have either a mild taste or none at all.

From the results, not yet complete, of the investigations hitherto made, it appears that glycerides are compounds if 1 At. glycerine, $C^6H^8O^6$, with 4 At. of a monobasic, or 2 At. of a bibasic acid, *minus* 8 HO. In the single case of Japan wax, however, only 4 HO are to be deducted.

All fats belonging to this class are resolved by contact with alkalis, magnesia, zinc-oxide, or lead-oxide, slowly in the cold, but more quickly with the aid of heat—the presence or absence of air being immaterial—on the one hand, into glycerine, which remains dissolved in the free state in the watery liquid, and on the other, into a fatty acid; or, if the fat itself consists of a number of simple fats, into several fatty acids, which unite with the salifiable base employed, and form with it, according to its nature, either soapy salts, as with potash and soda, or insoluble salts, having the consistence of plaster, as with the earthy alkalis and heavy metallic oxides. This decomposition is called *Saponification.*

The saponification of the various kinds of lard and suet takes place even when the air is completely excluded. It is not attended with formation of carbonic or acetic acid, but in the saponification of hog's lard, a small quantity of nitrogen is evolved (probably derived from animal impurities in the lard). 100 pts. of hog's lard digested with 60 pts. of potash-hydrate and 400 pts. of water for two days, at a temperature between 70° and 90°, are converted into mother-liquor and soap; the mother-liquor contains free potash, together with carbonate and acetate of potash, an odorous principle and glycerine; the soap contains stearate, margarate, and oleate of potash, a small quantity of acetate of potash, and yellow colouring matter. The carbonic acid, and the greater part of the acetic acid, found in the mother-liquor, were previously contained in the hydrate of potash, which had been purified by alcohol (III., 13); the remaining portion of acetic acid, which was extremely small, existed ready formed in the lard. 190 pts. of hog's lard saponified by potash, which had not been purified by alcohol, yielded 0·01 acetate of baryta; but after saponification with potash which had been purified by alcohol, the quantity of acetate of baryta obtained was 0·13. (Chevreul.)

To saponify 100 pts. of hog's lard requires 18 pts. of potash-hydrate, the product consisting of normal stearate, margarate, and oleate of potash, without excess either of acid or potash. (Excess of potash, however, renders the soap harder by abstracting water; carbonate of potash likewise hardens the soap, but not so much, and common salt still less.) When 100 pts. of lard are boiled for 60 hours, with 9 pts. of potash-hydrate and a small quantity of water, a homogeneous mass is obtained, almost wholly soluble in boiling alcohol, and forming a solution which does not redden litmus; but a large quantity of boiling water decomposes this mass into soluble soap and unaltered neutral fat; hence the potash saponifies exactly the quantity of fat which it can afterwards neutralize; and the soap thus produced forms with the excess of fat an emulsion, which does not produce grease-spots,—a property on which the power of soap to remove grease-spots chiefly depends. (Chevreul.)

$\frac{3}{5}$ pt. hydrate of soda, 1 pt. hydrate of baryta, strontia, lime, or lead-oxide, or $\frac{3}{5}$ pt. zinc oxide, heated for a considerable time with 1 pt. of lard and a proportionate quantity of water, decomposes the fat, just as potash does, into stearic, margaric, and oleic acid, which combine with the salifiable base, and glycerine (a small quantity of a yellow bitter principle being sometimes eliminated at the same time). (Chevreul.)

Hydrate of magnesia with water saponifies soap with the aid of heat; but the saponification takes several days, and even then is not complete. 1 pt. of ignited magnesia boiled for 100 hours with 1 pt. of lard and 6 pts. of water, combines with the lard, which is not perceptibly saponified, forming a solid, greyish yellow substance, whilst the water is found to contain no glycerin, but a small quantity of a bitter substance. Lard fused with an equal weight of ignited magnesia remains unaltered for two years, not even becoming rancid. (Chevreul.)

Saturated aqueous ammonia, kept in contact with hog's lard for 14 months, saponifies only $\frac{1}{15}$ of it, and if the liquid be then filtered till it passes through clear, and afterwards evaporated, it leaves glycerin, oleic acid, an orange-yellow colouring matter, and a trace of an acid soluble in water; the unsaponified lard has a somewhat pearly lustre, and contains a small quantity of oleic acid which may be extracted by cold alcohol. It appears then that lard is but very slowly saponified by ammonia at ordinary temperatures.—Hog's lard mixed with sublimed neutral carbonate of ammonia, and left in a bottle for 5 years, at a temperature below 18°, forms with water a white milk, containing pearly laminæ. This liquid, when heated, is resolved into three layers, the lowest of which is a watery liquid containing carbonate of ammonia and small quantities of oleic acid and glycerin mixed with margaric acid and yellow-colouring matter, the middle an oily, orange-yellow liquid, and the uppermost an oily, lemon-yellow liquid, which, as well as the middle layer, is a mixture of unsaponified fat with stearate, margarate, and oleate of ammonia. (Chevreul.)

1 pt. of hog's lard boiled with 2 pts. of bicarbonate of potash and with water, is almost wholly saponified; the unsaponified portion which floats on the soapy solution, may then be saponified by a second boiling with 1 pt. of bicarbonate of potash. The two portions of soap-solution being united and concentrated by evaporation, the liquid deposits all the soap, which, after being well pressed, is found to be free from carbonate of potash, whilst the mother-liquid contains the excess of carbonate of potash together with glycerin.—If the lard be saponified by monocarbonate of potash in a receiver standing over mercury, heat being applied

from without, no evolution of carbonic acid takes place till a considerable quantity of soap has been formed. When soap is saponified in the cold by excess of monocarbonate of potash, the liquid, after a while, deposits bicarbonate of potash.—Borax and biborate of potash, boiled for 50 hours with $\frac{1}{5}$ of their weight of lard and with water, saponify about 2 per cent. of the lard. (Chevreul, *Recherches*, 355.)

A simple fat, when saponified, yields glycerin and only one acid; but if the fat is a mixture of several glycerides, which is usually the case with natural fats, each of these yields its own peculiar acid; so that for every acid yielded by a fatty mixture, a corresponding fat may be supposed to exist therein.

The process adopted by Chevreul for separating these different fats is as follows:

Suppose the mixture contains a number of glycerides, the decomposition of which yields both volatile acids, such as valerianic, butyric, capric, caproic, and hircic acid; and fixed acids, such as stearic, margaric, and oleic acid, together with glycerin. Suppose, moreover, that it contains spermaceti, which is resolved by saponification into ethalic acid (mistaken by Chevreul for margaric acid), and, instead of glycerin, an unsaponifiable fat called ethal. 100 parts of this mixture are digested for a long time with 60 parts of potash-hydrate and 400 of water, till the whole is saponified, whereupon the above-mentioned acids combine with the potash. The liquid is then supersaturated with tartaric or phosphoric acid, and very gently heated till the more fixed acids, together with the ethal, rise to the surface in the form of an oil; after which the liquid is left to cool, the oil removed, and washed with water to free it from the acid liquid which adheres to it.

I. The mixture of the fixed acids and ethal is digested with baryta-water, till the acids contained in it are saturated with baryta; the liquid is then poured off, the mass dried, boiled with absolute alcohol or ether, and filtered.

1. The filtrate on evaporation deposits the ethal.

2. The baryta-salts insoluble in alcohol or ether are decomposed by dilute hydrochloric acid; the stearic, margaric, oleic (and ethalic) acids thereby separated, are dissolved in potash; the solution evaporated; the greater part of the oleate of potash extracted by absolute alcohol, &c.—(Further details respecting the separation of these acids will be given when we come to treat of them specially.)

II. The liquid separated from the fixed acids, which is mixed with the wash-water proceeding from the latter, and contains the volatile acids, together with glycerin and tartrate or phosphate of potash, is distilled.

1. The distillate saturated with baryta-water and evaporated, leaves valerianate, butyrate, caprate, caproate, and hircate of baryta, which must be separated by their different solubility in water, and their different tendency to crystallize. (See these acids.)

2. The residue of the distillation, evaporated to dryness in a basin, is treated with alcohol of sp. gr. 0·800, which leaves the greater part of the potash-salt undissolved, and after filtration and evaporation, yields glycerin, which may be freed from the remainder of the potash by a second solution in absolute alcohol, and filtration.

The products obtained by saponification amount, after thorough

drying, to 3 or 5 per cent. more than the fat from which they have been formed. Even if the resulting acids be calculated in the hypothetically anhydrous state, an excess of weight still appears. It must, therefore, be supposed, that, in saponification, a certain quantity of water is added, either as a whole or by its elements, to the constituents of the fat, in order to form the products of saponification.

Since the glycerides have no acid reaction, and, nevertheless, yield acids when acted upon by alkalis and other substances, their composition may be regarded in two different ways:—1. Either they are direct combinations of carbon, hydrogen, and oxygen; and alkalis endued with great affinity towards acids, induce these elements, by predisposing affinity, to take up, on the one hand, additional quantities of hydrogen and oxygen from the water, in such proportion as to produce acids, while, on the other hand, certain quantities of the three elements remain united in such proportions as to form glycerin.—2. Or, the glycerides contain acids and glycerin ready formed, *minus* a certain quantity of hydrogen and oxygen in equal numbers of atoms. They may be compared with ethers of the third class, which consist of an alcohol and an acid *minus* a certain quantity of HO. To this view Chevreul (*Recherches*, 442) rightly gives the preference. The quantities of glycerin and of fatty acid which form the glycerides, have been made out in a few cases only; but the researches of Chevreul and Lecanu upon stearin render it probable that this fat, by taking up 8 At. HO, is resolved into glycerin and 2 At. of bibasic stearic acid. We are, therefore, led by analogy to suppose that, when the fatty acid is monobasic, 1 At. glycerin corresponds to 4 At. of acid, and, accordingly, that the glycerides are copulated compounds of 1 At. glycerin with 2 At. of a bibasic, or with 4 At. of a monobasic acid, *minus* 8 At. HO. It is remarkable, however, that whereas ethers of the third class are neutral, because they contain only 1 At. of a monobasic acid to 1 At. of neutral substance, and copulated acids, on the contrary, are acid, because they contain 2 At. of acid, according to Gerhardt's law (p. 222), the glycerides exhibit a neutral character, although they contain 4 At. of monobasic acid. Whether this peculiarity can be satisfactorily explained by the feebly acid nature of the acids existing in the fats, and by the circumstance that they must be supposed to contain twice as many atoms of HO as can be separated from them, must, for the present, remain undecided. At all events, this difficulty need not compel us to suppose, as Gerhardt does, that the glycerides contain only 2 At. of a monobasic, or 1 At. of a bibasic acid, *minus* 6HO; for, in the first place, this assumption does not explain the neutral condition of the fats, inasmuch as it still admits the union of 2 At. of acid with 1 At. of a neutral body; and, secondly, it is controverted by the proportion of the glycerin to the soap-acid, as determined by Lecanu and Chevreul in the saponification of fats.

100 pts. of stearin yield 8 pts. of glycerin, dried as far as possible *per se*, and 96·86 pts. of stearic acid, also dried as much as possible *per se* (no other acid is produced at the same time). (Lecanu.)

The saponification-experiments of Chevreul agree for the most part with this result, although he did not use simple fats, but mixtures of stearin, margarin, and olein; for even his stearin still contained certain quantities of the two other fats, and similarly with his margarin and olein. Hence his stearin, when saponified, did not yield pure stearic acid, but a mixture of that acid with smaller quantities of margaric and oleic acid, the solidifying point of this mixture being so much farther

below that of pure stearic acid (from 66° to 70°,) as the quantities of margaric and oleic acid present were greater.

100 pts. yield	Glycerin.	Soap-acids.	Sum.	Freezing point of the acid mixture.
Stearin from Mutton suet	8·0	94·6	102·6	53°
——— Beef suet	9·8	95·1	104·9	52°
——— Hog's lard	9·0	94·65	103·65	52°
——— Goose fat	8·2	94·4	102·6	48·5°
Margarin from Butter	7·2	97·5	101·7	47·5°
Mutton suet	8·0	95·0	104·5	52°
Hog's lard	8·82	95·9	105·72	43°
Human fat	9·66	96·48	105·84	31°
Olein from Hog's lard	9·0	94·0	103·0	
——— Human fat	9·8	95·0	104·8	

The real excess is somewhat greater than that which the experiment shows, inasmuch as the preparation of the two saponification-products is always attended with a certain amount of loss. Even if the acids be supposed to exist in the fat in the hypothetically anhydrous state, there will still remain an excess of about 1 per cent.; hence the quantity of HO, which enters the product in saponification, is greater than that which is required to bring the soap-acid from the hypothetically anhydrous state to that in which it exists when dried *per se*. (Chevreul.)

The following comparative calculations render it probable that stearin is a compomnd of 1 At. glycerin with 2 At. of bibasic stearic acid ($C^{38}H^{67}O^{7}$), *minus* 8 At. HO. The calculation under *a* is based on this assumption;—that under *b* is similar, excepting that only 6HO are deducted;—that under *c* is likewise similar, but with deduction of only 4HO;—under *d*, the composition of stearin is calculated according to Gerhardt's hypothesis (viz., that stearin = 1 At. glycerin + 2 At. monobasic stearic acid, $C^{38}H^{38}O^{4}$ − 6HO).

a.			*b.*			*c.*			*d.*		
C	H	O	C	H	O	C	H	O	C	H	O
136	134	14	136	134	14	136	134	14	76	76	8
6	8	6	6	8	6	6	8	6	6	8	6
142	142	20	142	142	20	142	142	20	82	84	14
	8	8		6	6		4	4		6	6
142	134	12	142	136	14	142	138	16	82	78	8

From this the per-centage composition of stearin may be calculated as follows:—

According to *a*.			According to *b*.			According to *c*.		
142C	852	78·74	142C	852	77·46	142C	852	76·21
134H	134	12·39	136H	136	12·36	138H	138	12·34
12O	96	8·87	14O	112	10·18	16O	128	11·45
Stearin	1082	100·00		1100	100·00		1118	100·00

According to *d*.

82C	492	77·60
78H	78	12·30
8O	64	10·10
Stearin	634	100·00

	Chevreul.	Lecanu.	Liebig & Pelouze.
C	78·78	78·03	75·54 — 76·60
H	11·77	12·39	12·39 — 12·29
O	9·45	9·58	12·07 — 11·11
Stearin	100·00	100·00	100·00 — 100·00

	Arzbächer.	
	From Beef suet.	*From Mutton suet.*
C	78·62 — 78·95	76·18 — 76·68
H	12·22 — 12·43	12·17 — 12·50
O	8·83 — 9·19	11·03 — 11·54

The atomic weight of stearic acid in *a*, *b*, and *c* ($=C^{68}H^{67}O^{7}=531$; in *d*, according to Gerhardt's hypothesis ($C^{36}H^{35}O^{4}$), it is 298; the atomic weight of glycerin, $C^{6}H^{8}O^{6}$. From this we may calculate how much stearic acid and glycerin 100 parts of stearin would yield in saponification, according as its composition was that indicated in *a*, *b*, *c*, or *d*. In *a*, for example, we should have : 1082 : 2 . 531=100 : 98·15; and 1082 : 92=100 : 8·5. Hence we may calculate the following proportions. The data of Lecanu and Chevreul are likewise added.

	a.	*b.*	*c.*	*d.*	Lecanu.	Chevreul. (*at most.*)
Stearic acid	98·15	96·55	94·90	94·01	96·86	95·1
Glycerin	8·50	8·36	8·23	14·51	8·00	9·8
Sum	106·65	104·91	103·13	108·52	104·86	104·9

On comparing these calculations with the experimental data, it appears that Gerhardt's view, *d*, is inadmissible, since, according to this calculation, stearin should yield a quantity of glycerin larger than any that has been obtained from it. The theory *c* gives too little stearic acid, and an improbable per-centage composition of the stearin; the choice lies therefore between *a* and *b*. The theory *b* appears at least to have this in its favour—that the quantity of stearic acid obtained by Lecanu and Chevreul agrees with it better than with *a*. If, however, we take into consideration that a loss of stearic acid is scarcely to be avoided in this experiment, so that the quantity obtained ought rather to be in defect than in excess, but that Lecanu (who examined the purest stearin) obtained rather more stearic acid than would be possible, according to calculation *b*—and if we further compare Chevreul's analysis of stearin with its composition as calculated according to *a* and *b*—we must certainly give preference to the hypothesis *a*, according to which 8HO are separated. It is true that this hypothesis does not agree with the oft-repeated analysis of Liebig and Pelouze (*Ann. Pharm.* 19, 204), according to which stearin does not contain more than 76·6 per cent of carbon; whence these chemists were led to regard stearin as a compound of 2 At. stearic acid ($=2C^{70}H^{66}O^{7}$) with 1 At. glycerin, *minus* 3HO, or, which comes to the same thing, as a compound of 2 At. hypothetically anhydrous stearic acid ($=2C^{70}H^{67}O^{5}$), with 1 At. hypothetically anhydrous glycerin ($=C^{6}H^{7}O^{5}$), and 2 At. HO. But, according to this hypothesis, 100 parts of stearin should yield only 94·37 stearic acid and 7·96 of glycerin. Liebig (*Chim. org.* 2, 193) remarks that the stearin analyzed by himself in conjunction with Pelouze was not quite pure; and the analysis was made with oxide of copper only. Such being the case, one cannot but wish that these two distinguished chemists would repeat their analysis with perfectly pure stearin; as the repetition might perhaps remove the only weighty objection which prevents the hypothesis *a* from being received.

¶ Arzbächer's analysis (*Ann. Pharm.* 70, 239) above quoted seems to show that beef-stearin has the composition *a;* viz., 1 At. glycerin + 2 At. bibasic stearic acid − 8HO, and mutton-stearin the composition *c;* viz., 1 At. glycerin + 2 At. bibasic stearic acid − 4HO. These results have been discussed by Laurent & Gerhardt (*Compt. mensuels*, 1849, 343), who now regard stearic acid as isomeric (not polymeric) with margaric acid, and therefore assign to it the formula $C^{34}H^{34}O^4$. With this formula for stearic acid, they consider beef-stearin as a compound of 1 At. glycerin + 2 At. stearic acid − 8HO = $C^6H^9O^6 + 2C^{34}H^{34}O^4 - 8HO = C^{74}H^{68}O^6$ (which formula requires 79·2 p. c. carbon and 12·1 hydrogen), and mutton-stearin as a compound of 1 At. glycerin + 2 At. stearic acid − 6HO = $C^{74}H^{70}O^8$ (which requires 76·8 p. c. carbon and 12·1 hydrogen) (vid. *Jahresber.* 1849, 341).

In order to make this comparative examination as extensive as possible, the other fats which have been most minutely examined, are likewise calculated in the same manner as above, according to *a* and *b;* and in the case of palmitic acid, likewise according to *c*, and the results collected in the following tables. As these other fats yield monobasic acids, 4 At. acid are added to 1 At. glycerin, and 8, 6, or 4 At. HO substracted from the result. In these calculations, the composition of the soapy acids is expressed by the following formulæ: Margaric acid = $C^{34}H^{34}O^4$; — Oleic acid = $C^{36}H^{34}O^4$; — Linoleic acid = $C^{30}H^{24}O^4$; — Palmitic acid = $C^{32}H^{32}O^4$; — Myristic acid = $C^{28}H^{28}O^4$; — Laurstearic acid = $C^{24}H^{24}O^4$. — Under each per-centage calculation of a fat are placed the quantities of acid and glycerin which 100 parts of it would yield by saponification.

Margarin (8HO)			(6HO)		
142C	852	77·45	142C	852	76·21
136H	136	12·37	138H	138	12·34
14O	112	10·18	16O	128	11·45
	1100	100·00		1118	100·00
Margaric acid		98·22		96·60	
Glycerin		8·36		8·23	

100 parts of impure margarin from butter yields 94·5 pts. of acid and 7·2 of glycerin; 100 parts of human fat (a mixture of margarin and olein) yield 96·18 acid and 9·66 glycerin. (Chevreul.)

Olein (8HO)			(6HO)			*From human fat.* Chevreul.
150C	900	78·40	150C	900	77·19	78·57
136H	136	11·84	138H	138	11·83	11·45
14O	112	9·76	16O	128	10·98	9·98
	1148	100·00		1166	100·00	100·00
Oleic acid		98·26		96·74		
Glycerin		8·01		7·86		

Drying oil (8HO)			(6HO)			*Linseed-oil (containing Margarin).* Sacc.
126C	756	78·42	126C	756	76·99	78·12
96H	96	9·96	98H	98	9·98	10·96
14O	112	11·62	16O	128	13·03	10·92
	964	100·00		982	100·00	100·00
Linoleic acid		97·93		96·13		
Glycerin		9·54		9·37		

Palmitin (8HO)			(6HO)			(4HO)		*Palmitin.* Stenhouse.	*Japan wax.* Sthamer.	
134C	804	77·01	134C	804	75·71	134	804	74·45	76·67	73·95
128H	128	12·26	130H	130	12·24	132	132	12·22	12·18	11·85
14O	112	10·73	16O	128	12·05	18	144	13·33	11·15	14·20
	1044	100·00		1062	100·00		1080	100·00	100·00	100·00
Palmitic acid		98·08			96·42			94·81		
Glycerin		8·81			8·66			8·52		

Both palmitin, which melts at 48°, and Japan wax, which melts at 42°, are resolved by saponification into glycerin and palmitic acid. The difference between them appears to be, that in palmitin 8HO are abstracted, and in Japan wax only 4HO.

Myristin (8HO)			(6HO)			Playfair.	
118C	708	75·96	118C	708	74·53	75·43	
112H	112	12·02	114H	114	12·00	12·26	
14O	112	12·02	16O	128	13·47	12·31	
	932	100·00		950	100·00	100·00	
Myristic acid		97·85			96·00		
Glycerin		9·87			9·69		
Laurostearin (8HO)							
102C	612	74·63	102C	612	73·03	73·88	74·01
96H	96	11·71	98H	98	11·69	11·65	11·36
14O	112	13·66	16O	128	15·28	14·47	14·63
	820	100·00		838	100·00	100·00	100·00
Laurostearic acid		97·56			95·47		
Glycerin		11·22			10·98		

On comparing the analyses of these fats with their calculated composition, it becomes more and more probable that in most of them 8HO are eliminated, but in Japan wax only 4HO; that is to say, exactly half the usual quantity.

(For Chevreul's calculation of the relation which the composition of fats bears to their saponification-products, see his *Recherches*, 322;—Fechner's calculation; *Kastn. Arch.* 12, 336;—Gusserow's; *Kastn. Arch.* 19, 69, and 219.)

If we further assume—which however must be looked upon as a mere fiction—that in these fats 4HO are abstracted from the glycerin, and 4HO from the 4 atoms of acid, the formula of margarin, for example, may be written: $C^6H^4O^2,4C^{34}H^{33}O^3$. This glycerin-residue, $C^6H^4O^2$, would have the composition of acrolein, a substance usually obtained in the dry distillation of glycerides; but we have no more reason to suppose that the fats actually contain ready-formed acrolein than that ether is contained in oxalic ether, to which we assign the formula $2C^4H^5O,C^4O^6$. The acrolein is present only by its elements, the atoms being arranged in a different way. This view is supported by Redtenbacher's observation (*Ann. Pharm.* 47, 138), that whereas acrolein, when acted upon by an alkali, is immediately converted into a resin, the glycerin-residue of fats is immediately converted in saponification into glycerin.

The copulated nature of the glycerides is likewise corroborated by the following observations:

1. Olive-oil heated with one-fourth its weight of peroxide of manganese, gives off carbonic acid, and yields a manganous soap. (Scheele,

Opusc. 1, 261.) In this reaction the excess of oxygen decomposes the glycerin-residue; whilst the manganous oxide combines with the margaric and oleic acid. (Liebig & Pelouze, *Ann. Pharm.* 19, 268.)—Oxide of lead digested with a glyceride at 100°—110°, without any water, yields, without loss of weight, a lead-soap containing very little glycerin, but a very large quantity of acetate of lead. The acetic acid is derived from the decomposed glycerin-residue. (Gusserow, *Kastn. Arch.* 19, 69.)

2. When dry hydrochloric acid gas is passed through a heated solution of castor-oil in absolute alcohol, the liquid shaken up with water, and the turbid mixture set aside, it separates into a watery and an oily layer. The former, evaporated over the water-bath, gives off hydrochloric acid, and leaves a yellowish syrup, which, when treated with ether, leaves glycerin, whilst the ethereal solution yields, on evaporation, oily drops, consisting of a mixture of the compound ethers of the acids contained in the castor-oil; hence the copulated compound of the soapy acids with glycerin has been converted into a compound of the same acids with ether. (Rochleder, *Ann. Pharm.* 59, 260.) [What does the oily layer consist of?]

Oleate of lead digested for 24 hours with margarin from palm-oil or goose-fat, the mixture being frequently stirred and kept at a temperature between 100° and 110°, acquires a much firmer consistence, because it is converted into margarate of lead, and consequently the margarin is replaced by olein. No glycerin is set free. (Gusserow, *Kastn. Arch.* 19, 219.)

Glycerides may be divided into those which yield volatile acids by saponification, and those which yield fixed acids.

In the following table are given the name and composition of the acid yielded by each fat, and, so far as they are known, the melting points of the fat and of the acid.

1. *Fats which yield Volatile Acids.*

		C	H	O
Butyrin	Butyric acid	8	8	4
Valerin *or* Delphinin	Valerianic acid	10	10	4
Caproin	Caproic acid	12	12	4
Caprylin	Caprylic acid	16	16	4
Caprin	Capric acid	20	20	4
Hircin	Hircic acid			
Sabadillin	Sabadillic acid			
Crotonin	Crotonic acid			
Ricinin	Ricinic acid			

2. *Fats which yield Fixed Acids.*

Laurostearin	45°	Laurostearic acid	24	24	4		43°
Cocosin	22	Cocinic acid	26	26	4		35
Myristin	31	Myristic acid	28	28	4		49
Benin		Benic acid	30	30	4		43
Moringin		Moringic acid	30	28	4		0
Drying fat or Linolein		Linoleic acid	30	24	4		
Palmitin	48	Palmitic acid	32	32	4		60
Butyrolein		Butyroleic acid					
Ricinolein		Ricinoleic acid					
Olein		Oleic acid	36	34	4		4
Elaidin	36	Elaidic acid	36	34	4		44
Margarin	49	Margaric acid	34	34	4		58
Stearin	61	Stearic acid	68	67	7		70
Margaritin		Margaritic acid					130

Several of these fats are not known in the separate state; their existence is merely inferred from the formation of their fatty acids in the saponification of certain mixed fats.—In general, the melting point of a fat is somewhat lower than that of the corresponding acid.

Decompositions of Glycerides which yield Volatile Soap-acids.

As these fats are not yet known in the pure state, but are always mixed with at least an equal quantity of olein, the following observations respecting them may suffice. They are much more easily resolved into their constituent elements than the fats of the more fixed acids. On mere exposure to the air, they gradually give off their volatile acid, from which they derive their odour and their power of reddening litmus; the decomposition is more quickly effected by boiling with water or with hydrated alcohol. Oil of vitriol, by taking up the glycerin of these fats, likewise sets free the volatile acids. These fats appear also to saponify more readily than the others.

Decompositions of Glycerides which yield Fixed Acids.

Dry Distillation. Fats begin to boil at about 300°, but volatilize in a state of almost complete decomposition, the boiling point of the residue continually rising. They cannot therefore be said to have any fixed boiling points. At the commencement of the distillation, marsh-gas, olefiant gas, carbonic oxide, and a small quantity of carbonic acid, are evolved, and a distillate is obtained, the nature of which changes as the distillation goes on. The distillate obtained at the beginning of the process contains the following products: 1. Part of the acid which the fat would yield in saponification, or a similar acid. Thus stearin yields margaric instead of stearic acid; and olein yields sebacic as well as oleic acid.—2. Acrolein, $C^6H^4O^2$, which imparts to the distillate its extremely pungent and repulsive odour, and acrylic acid, $C^6H^4O^4$, apparently resulting from the decomposition of glycerin.—3. A small quantity of acetic acid, which, according to Redtenbacher's suggestion, is formed from acrylic acid by the action of water.—4. Oily aldides, such as creosote and œnanthol. —5. Numerous hydrocarbons, which generally appear to contain C and H in equal numbers of atoms, some being oily, like eupione, oleene, and elaene; others solid, like paraffin.—As the heat is continued, the acid distillation-products diminish, and the empyreumatic oils increase in quantity; so that at length a distillate is obtained which does not redden litmus, and from which aqueous potash extracts nothing.—The residue in the retort becomes continually thicker, swells up, chars, and when the retort attains a commencing red heat, gives off yellow vapours, which sublime like chrysene or some substance of like nature. From 1 to 4 per cent. of charcoal is left behind.—One part of the acid residue contained in the fat abstracts from the remainder the quantity of H and O necessary to convert it into the ordinary acid, and in that state passes over, chiefly at the beginning of the distillation, as an oily liquid which in most cases solidifies on cooling; while the other part of the acid residue, which has given up the HO, passes over at a subsequent stage of the distillation as a permanently fluid mixture of various hydrocarbons.—On distilling fat mixed with a large quantity of clay or brick-dust, whereby the volatiliza-

tion of the first products is mechanically retarded, these products are decomposed by the stronger heat to which they are exposed, and the ultimate product contains less soap-acid and more empyreumatic oil.

Decomposition at a red heat. When a fat is made to pass in drops through an iron tube at a low red heat, whereby it is subjected to a stronger heat than in distillation, it yields but a small quantity of liquid products of decomposition, but is for the most part resolved into a mixture of gases, called *Oil-gas*, which, of all gases that are used for illumination, gives out the greatest quantity of light in burning. It is a mixture of carbonic oxide, hydrogen, marsh-gas, olefiant-gas, the vapours of two empyreumatic oils (probably C^8H^8 and $C^{16}H^{16}$) and benzin $C^{12}H^6$.—In this decomposition, the oxygen of the fats appears to pass almost wholly into carbonic oxide.

Slow combustion. Fats which are liquid at the medium temperature of the air, absorb oxygen from the air at this temperature, exhibiting, in consequence, the phenomena of *thickening*, *turning rancid*, and *spontaneous combustion*.—Fats of the stearin class undergo, when pure, no perceptible alteration in the air; but when, as generally happens, they are mixed with oily fats, they exhibit alterations similar to the latter. Even the pure solid fats, if exposed for some time to the air at their melting points, would probably exhibit similar changes.

Fixed oils enclosed in oxygen gas absorb the gas very sparingly for the first 4 or 6 months, but afterwards very abundantly, the absorption going on for 4 years, after which it ceases, partly for want of oxygen. The oils, during this action, give off carbonic acid and carburetted hydrogen gas [or perhaps a mixture of hydrogen with smaller quantities of marsh-gas and carbonic oxide]. In four years, 1 volume of drying oil absorbed about 160 volumes of oxygen, and evolved about 24 volumes of carbonic acid and 7 volumes of carburetted hydrogen; and 1 volume of non-drying oil absorbed 120 vol. oxygen, and gave off 25 vol. carbonic acid together with 6 vol. carburetted hydrogen. (Saussure, *Pogg.* 25, 364.)

The thickening of the fixed oils is intimately connected with the absorption of oxygen, but this absorption appears to have little to do with turning them rancid. The latter effect appears to accompany the action of the air on large masses of the oils, chiefly when they are contaminated with animal cellular tissue, emulsin, gluten, and other protein-substances, which putrefy on exposure to the air, and act as ferments in bringing the oils into a state of rancid decomposition. Hence oils may be preserved by Appert's process, viz., by placing bottles completely filled with them in water; keeping the water for some hours at the boiling heat; and closing the bottles tightly during the application of the heat. Oils become rancid more quickly when exposed to light, especially to sunshine, than in the dark (*comp.* Save, *Bull. Pharm.* 5, 20). They then become more viscid, almost like turpentine, and yield a neutral odorous principle, one or more volatile acids, and the same acid which is produced from them in saponification, whereby they acquire an offensive taste and smell, and the property of reddening litmus.

Hog's lard, spread over the sides of a vessel filled with oxygen gas, and left to itself for three years in a situation not exposed to sunlight, absorbs the greater part of the oxygen, evolving, however, little or no carbonic acid, becomes white, and smells very rancid, aromatic, and sour. If it be washed repeatedly with water, the liquid distilled, the rancid-smelling, acid distillate saturated with baryta-water and distilled again,

the second distillate is not acid, but smells rancid, and after long keeping exhales the odour of Roquefort cheese. The resulting baryta-salt contains an acid like capric acid, and perhaps also another. In the aqueous residue of the first distillation, drops of oleic acid float, tinged with an orange-yellow colouring matter; the distillate itself is yellow, has a sour and bitter taste, and contains a fixed acid soluble in water, a yellow colouring matter, and perhaps also an organic substance not possessing acid properties. When the rancid hog's lard, after being thus washed with water, is boiled with alcohol of sp. gr. 0·82, then cooled, and afterwards thrown on a filter, it leaves on the filter a quantity of stearin, together with more or less olein; the filtrate yields, on evaporation, a very acid, oily residue, from which boiling water extracts an orange-yellow colouring matter; and if the residue be boiled with magnesia and water, the water removed, and the solid matter afterwards boiled with alcohol, a quantity of neutral fat is dissolved out, and a mixture of oleate, margarate, and probably also stearate of baryta, remains behind. Hence it appears that hog's lard, in turning rancid, yields the following products: a volatile, neutral substance having a rancid odour, and similar to that which is produced in the dry distillation of fats [acrolein]; a volatile acid similar to caproic, and perhaps also another volatile acid, which also contribute to produce the rancid odour; oleic, margaric, perhaps also stearic acid; a yellow colouring matter, and a neutral non-volatile substance, soluble in water. (Chevreul, *Recherches*, 453.)

The rancid odour and taste of spoiled fats may be removed, sometimes by merely heating them with an equal quantity of water; sometimes by boiling them with water and magnesia, till the liquid no longer reddens litmus, then straining through linen, and washing with water (Köhnke, *N. Br. Arch.* 39, 296); sometimes again by soaking them thoroughly in dilute chloride of potash (Charlot, *J. Pharm.* 17, 357) or chloride of lime (Bonastre and Labaraque, *J. Pharm.* 17, 359), and afterwards washing with water.

Drying oils exposed to the air in thin layers, dry up to an elastic resinous substance; non-drying oils are converted, by similar treatment, into a tenacious, greasy mass.

When porous substances are saturated with fixed oils, so that the oil presents a very large surface to the air, the absorption of oxygen takes place more quickly; the development of heat which accompanies it accelerates the process; this again produces a more rapid evolution of heat, by which the oxidation is still further accelerated; and at last, when the mass is considerable, the temperature rises to the point at which rapid combustion takes place.

This spontaneous combustion of fixed oils, which is a frequent cause of fires, occurs more readily with drying than with non-drying oils. It takes place in intervals varying from a few hours to four weeks, when considerable masses of lamp-black, tow, linen, paper, cotton, calico, wool, woollen stuffs, ship's cables, wood-ashes, ochre, &c., are slightly soaked in oil, and packed in such a manner, that the air has moderate access to them: a rapid change of air exerts a cooling action (*comp.* Sommer, *Gilb.* 63, 426; Hagen, *Gilb.* 63, 439; Bizio, *Brugn. Giorn.* 13, 184; *Mag. Pharm.* 7, 155; *Scher. Ann.* 3, 419; Kastner, *Kastn. Arch.* 5, 208; Mease, *Sill. Amer. J.* 33, 147 and 199; Ritz, *N. Br. Arch.* 39, 264; also Graham's Chemical Report on the cause of the Fire in the "Amazon," *Chem. Soc. Qu. J.* 5, 34). Many kinds of ochre take fire during the process of trituration with fixed oils. (Mease.)—A mixture of minium and

linseed-oil, which had been kept for some years, took fire while being pulverized (*Phil. Mag. J.* 11, 324).—The vegetable residue left after the preparation of *Olea cocta* often exhibits spontaneous combustion (*Mag. Pharm.* 7, 158; Boissenot, *Ann. J. Pharm.* 8, 133; 10, 191; Boulogne, *J. chim. méd.* 22, 672).—The trimmings of lamp-wicks kept in an open wooden box have been known to take fire. (Thénard, *Compt. rend.* 23, 840.)—If a round hole be made in a large lump of *Magnesia alba*, and smeared with boiled and still warm linseed-oil, till its sides are saturated to the thickness of $\frac{1}{4}$ of a line, a strong smell of linseed-oil and great heat are perceptible in the aperture after the lapse of an hour—then a thick smoke—and, after an hour and a half, the sides exhibit a bright red heat, which continues till the oil is completely burned. (Pflugfelder, *Repert.* 56, 97.)

Rapid combustion. Fats, in consequence of their higher boiling points, require a stronger heat to set them on fire than the greater number of volatile oils. They burn with a very bright, white flame, which deposits no soot, unless the supply of air be insufficient.—The wick facilitates the combustion, inasmuch as the oil which rises through it can more readily be brought to the temperature required to set it on fire. (Respecting the nature of a candle-flame, *comp.* II., 30.) In the Argand lamp, the current of air is stronger, and the oily vapour is not compelled to rise so high, in order to receive the quantity of oxygen necessary to burn it; hence the flame is shorter but more concentrated; and the particles of soot being brought to a stronger white heat, give out a brighter light. But the portion of light which can diffuse itself through the space required to be illuminated is almost wholly confined to the outer surface of the cylinder of oily vapour which rises from the wick; of that which is produced in the interior, a considerable quantity is lost. If, then, by a suitable construction, as in Benkler's so-called gas-lamp, the inner current of air can be retarded (being, however, kept strong enough to prevent flickering) and the outer current strengthened, so that the greater portion of the oil shall be burned on the outside, a given quantity of oil may be made to produce a much greater quantity of light.

That fats undergo slow combustion below the temperature at which they take fire, is shown by the following observations: When a fixed oil or wax is placed upon a piece of metal heated to a temperature much below redness, slow combustion takes place, accompanied by a peculiar odour and a luminosity perceptible in the dark; similarly, when a candle having its wick well saturated with tallow, is blown out in such a manner as to leave the wick at a heat below redness. (Charles & Williams, *Phil. Ann.* 6, 44;—*comp.* also Dessaignes and Williams, I., 200, 201.)—Tallow heated in an open spoon till it takes fire, then blown out and plunged into oxygen gas, bursts into flame again. (Graham, *Elements of Chemistry.*)

Chlorine, Bromine, and *Iodine* decompose fats by forming substitution-products, which have as yet been but little examined.

Fuming nitric acid sets fire to drying fatty oils; a mixture of this acid with oil of vitriol sets fire even to olein; but solid fats are but slowly decomposed by fuming nitric acid.—When fats are heated for some time with dilute nitric acid, the products of decomposition are the same that would be formed by the action of nitric acid on a mixture of glycerin and the soap-acid of the fat. Thus, glycerin yields oxalic, and

perhaps also acetic acid; and the soap-acid is converted by progressive oxidation, first into a resinous mass, then into various other acids, such as suberic, pimelic, adipic, lipic, succinic, and others, differing according to the nature of the original acid.—When weak nitric acid acts for a shorter time on fats, its decomposing action is exerted almost wholly on the glycerin-residue, the soap-acid of the fat being set free, occasionally in a somewhat altered state.

Oil of Vitriol at high temperatures browns and blackens fats, giving off sulphurous and sometimes also formic acid, and forming a resinous matter, a substance like tannin, and a coaly substance, all of which appear to contain sulphuric acid. When oil of vitriol is very gently heated with twice its weight of fat, it unites with the glycerin-residue, forming sulphoglyceric acid, while the soap-acid of the fat remains behind.

Combinations of Glycerides.—All glycerides are perfectly insoluble in water.—A. Fats in the liquid state absorb various gases.—B. Fats in the liquid state dissolve phosphorus, and thereby acquire the property of shining in the dark.—C. Fats in the liquid state dissolve sulphur.—Fats are soluble in sulphide of carbon.—D. They may be made to unite with selenium by fusion.—E. In the liquid state they dissolve iodine, which then exerts a gradual decomposing action upon them.—F. They mix with the chlorides of phosphorus and sulphur.—They are not soluble in aqueous ammonia; but liquid fats form with it a white pasty mixture which takes a long time to separate: *Liniment.*—G. Fats in the liquid state dissolve certain metallic oxides, such as arsenious-acid, arsenic acid, lead-oxide and cupric oxide, the combination being, however, probably attended with some decomposition. Many fats likewise mix with chloride of arsenic.—H. Fats are miscible with various organic acids, especially with those which contain but little oxygen, *e. g.*, stearic, oleic, suberic, camphoric, and benzoic acid; they likewise take up a small quantity of oxalic acid.—I. Most fats dissolve but sparingly in alcohol, wood-spirit, or acetone. According to Saussure, they are more soluble in alcohol, in proportion as they contain more oxygen; hence also a fixed oil becomes more soluble in alcohol, as it oxidizes by exposure to the air. Ether dissolves most fats more abundantly than alcohol; and volatile oils mix with them with great facility. Fats likewise dissolve camphors, and the greater number of resins, resinous colouring matters, and alkaloids. Glycerides likewise mix with most other bodies included in the class of fats, as well as with each other.

¶ *Isomeric transformations of Glycerides.*—Heintz observed that mutton-stearin, enclosed in a capillary tube and heated in the water-bath, becomes perfectly transparent at 51° or 52°, opalescent at a somewhat higher temperature, resumes its opacity at about 58°, and fuses at 62°—62·5° A thin film of stearin, immersed in water, becomes perfectly transparent at 51°—52°, without changing its form (*Ber. Ber. Acad.* 1849, 222; *Pharm. Centr.* 1850, 188; *Instit.* 1849, 390; *Jahresber.* 1849, 342).

These phenomena have been more minutely examined by Duffy (*Chem. Soc. Qu. J.* 5, 197), who finds that stearin is susceptible of three isomeric modifications, each of which is distinguished by a peculiar melting point. When gradually heated, it melts at the temperature of the first of these points (about 51°), then solidifies; melts at the tempera-

ture of the second, solidifies; melts at the temperature of the third (about 69°), and then solidifies only when the temperature has fallen below all three. After solidifying at this point, it may be made to melt again at the first, second, and third melting points respectively, solidifying as before, below all three; and these changes are producible in this succession to any extent, without the slightest loss or gain of weight. As the stearine approaches to purity (by repeated crystallization from ether), the interval between the first and second melting points diminishes; hence it is probable that perfectly pure stearin* (which has never yet been obtained) would exhibit only two melting points, those, namely, which are here called the first and third.

The three modifications also differ in density, the first being lighter, the second and third heavier than water; at 15°, the density of the first is 0·9867, of the second 1·0101, of the third 1·0178. These numbers apply to mutton-stearin crystallized 32 times from ether, and having its third melting point at 69·7°.

Similar modifications are exhibited by other glycerides, viz., stearin from beef-fat, a glycerin-fat from a kind of vegetable tallow (the history of which is not exactly known), palmitin and margarin. The following table exhibits the melting points of these fats:

	Solidifying points.	*Melting points.* (1)	(2)	(3)
Mutton-stearin	51·7°	52·0°	64·2°?	69·7°
Beef-stearin	50·5	51·0	63·0	67·0
Substance from vegetable tallow	45·0	45·0	62·0	64·5
Palmitin from palm-oil	45·0	46·0	61·7	62·8
Margarin from butter	40·0	40·5	51·0	52·6
Margarin (?) from human fat	43·5	44·2	54·5	56·0

The property of existing in two, if not three modifications, appears not to belong to any fatty substances excepting the glycerin-fats: at all events the acids derived from them do not possess it; neither is it exhibited by stearic or cerotic ether, cerotin, cerotene, Chinese wax or paraffin. ¶

* The purest stearin which Duffy obtained had been crystallized 32 times from ether, and amounted to only 8 grammes from 2 kilogrammes of the crude fat; it still, however, appeared to be not quite pure; for the residue of the mother-liquid differed in melting point by 2° from that which crystallized out.

COMPOUNDS CONTAINING 2 AT. CARBON.

METHYLENE SERIES.

A. Primary Series.

A. Primary Nucleus. Methylene, C^2H^2.

Syn. *Forme, Palen* (the term *Methylene* is derived from *μέθυ, wine*, and *ὕλη, wood*), *vid.* p. 258.—Obtained in 1835 by Dumas and Péligot (*Ann. Chim. Phys.* 58, 28), but not accurately known. Regnault (*Ann. Chim.* 71, 427) doubts the existence of methylene, inasmuch as it is not obtained by treating methyl-ether, C^2H^3O, or wood-spirit, $C^2H^4O^2$, with excess of oil of vitriol. ¶ The decomposition of hydrated oxide of tetramethylium might be expected to yield methylene, just as that of the hydrated oxide of tetrethylium yields olefiant gas (p. 180); but there appears to be something peculiar in the decomposition which prevents the separation of this compound. (Hofmann.) ¶

Preparation. Gaseous hydrochloric methyl-ether, C^2H^3,HCl, is passed in the dry state through a porcelain tube kept at a cherry-red heat; and the resulting gas is freed, by agitation with a large quantity of water, from the hydrochloric acid gas produced at the same time, and from the undecomposed portion of the ether, the washing being continued till the gas burns without formation of hydrochloric acid.—As a certain portion of charcoal is deposited in the tube, the gas thus obtained cannot be considered quite pure.

Colourless gas, having no reaction on vegetable colours.

				Vol.	Density.
2C	12	85·71	C-vapour	2	0·8320
2H	2	14·29	H-gas	2	0·1386
C^2H^2	14	100·00	Methylene-gas	2	0·9706
				1	0·4853

The gas when set on fire in the air burns with a yellow flame; 2 volumes of it burnt in the detonating eudiometer with excess of oxygen gas, consume 3 volumes of oxygen and produce 2 volumes of carbonic acid. The 2 vol. C-vapour unite with 2 vol. O, forming 2 vol. CO^2; and the 2 vol. H unite with 1 vol. O and form water.—Chlorine does not act upon this gas in the shade, but combines with it in sunshine. (Dumas and Péligot.)

Methyl. $C^2H^3 = C^3H^2,H$?

FRANKLAND & KOLBE. *Chem. Soc. Qu. J.* 1, 60; *Ann. Pharm.* 65, 251.
KOLBE. *Chem. Soc. Qu. J.* 2, 173; *Ann. Pharm.* 69, 279.
FRANKLAND. *Chem. Soc. Qu. J.* 2, 297; *Ann. Pharm.* 71, 213; *N. Ann. Chim. Phys.* 29, 253.

This compound was first obtained by Kolbe in 1849, by the electrolysis of acetic acid; Frankland afterwards obtained it by the action of zinc on iodide of methyl. The gas which Frankland and Kolbe had previously obtained, in 1848, by decomposing cyanide of ethyl with potassium, and which they at first regarded as methyl, C^2H^3, is now considered by Frankland to be the hydride of ethyl, $C^4H^5,H = C^4H^6$.

Preparation. By the Electrolysis of Acetic acid.—When a concentrated solution of acetate of potash is subjected to the action of the electric current, a number of gaseous products are evolved; viz., carbonic acid, hydrogen, an inflammable, inodorous gas, and a gas which smells like ether; the last is completely absorbed by sulphuric acid (if the smallest quantity of chloride of potassium be present in the solution, chloride of methyl is formed). The gaseous mixture thus evolved, after being freed from carbonic acid, contained in one experiment, in 100 volumes: 0·7 vol. oxygen, 63·8 hydrogen, 32·6 methyl, 2·1 oxide of methyl, 0·8 acetate of methyl; in another experiment, 66 vol. hydrogen were obtained to 28 methyl. If the solution of acetate of potash be divided by a porous diaphragm, so that the gases evolved at the two poles may be collected separately, nothing but hydrogen is evolved at the negative pole, while at the positive pole there is evolved a gaseous mixture, which, after being treated with potash and with sulphuric acid, leaves nothing but methyl mixed with a small quantity of oxide of methyl. (Kolbe.) The decomposition is expressed by the following equation (*comp.* p. 171):

$$C^4H^4O^4 = C^2H^3 + 2CO^2 + H.$$

Methyl thus prepared (mixed with traces of the oxide) is an inodorous and tasteless gas, insoluble in water, and burns with a bluish flame, which gives but little light. Alcohol dissolves an equal volume, absorbing it without residue. It is not dissolved by sulphuric acid or by pentachloride of antimony. (Kolbe.) These properties are likewise possessed by the gas obtained by decomposing cyanide of ethyl with potassium; hence Kolbe considered the two identical. Frankland, however, as already observed (p. 172), regards them as merely isomeric.—Methyl does not liquefy at −18°.

				Vol.	Density.
2C	12	80	C-vapour	2	0·8320
3H	3	20	H-gas	3	0·2079
C^2H^3	15	100	Methyl-gas	1	1·0399

The density of the gas obtained from cyanide of ethyl by potassium was found by experiment to be 1·075 (Frankland & Kolbe), (it contained a little of the heavier vapour of the cyanide). The density of the gas produced by the electrolysis of acetic acid and by the action of zinc on iodide of methyl, does not appear to have been directly determined; but that of a mixture of 26 vol. CO^2, 69·3 vol. methyl, and 4·7 vol. oxide of methyl (obtained by electrolysis of acetic acid), which by calculation

should be 1·192, was found by experiment to be 1·172. (Kolbe, *Chem. Soc. Qu. J.* 2, 182.)—[For the discussion respecting the vapour-volume of methyl and the other organic radicals, vid. pp. 171-174.]

1 vol. methyl requires for complete combustion $3\frac{1}{2}$ vol. oxygen (2 vol. C-vapour require 2 vol. O, and 3 vol. H require $1\frac{1}{2}$ vol. O), and yields 2 vol. carbonic acid gas,—1 vol. chlorine and 1 vol. methyl yield 1 vol. hydrochloric acid gas and 1 vol. of a gas having the formula C^4H^5Cl; and the same action is exerted by chlorine on an equal volume of the hydride of ethyl obtained by the action of potassium on cyanide of ethyl. It is most probable, however, that in the former case, the chlorine acts on only half the methyl, yielding a mixture of methyl, C^2H^3, hydrochloric acid, HCl, and another gas having the composition $C^2(H^2Cl)$, or, methyl with 1 At. Cl. substituted for H: thus,

$$2C^2H^3 + 2Cl = C^2H^3 + C^2(H^2Cl) + HCl.$$

A mixture of C^2H^3 and C^2H^2Cl is evidently equivalent in composition to C^4H^5Cl.—When 2 vol. chlorine are mixed with 1 vol. methyl, the products are, in fact, 2 vol. HCl. and 1 vol. of a gas having the composition C^2H^2Cl. But when 2 vol. chlorine are mixed with 1 vol. hydride of ethyl, 2 vol. hydrochloric are produced, together with an oily liquid having the same per-centage composition as Dutch liquid, $C^4H^4Cl^2$. From these results Frankland concludes that the two gases above-mentioned, the one obtained by the electrolysis of acetic acid or by the action of zinc upon iodide of methyl, the other by the action of potassium on cyanide of ethyl,—are really different, the one being the true radical methyl, C^2H^3, and the latter, hydride of ethyl, C^4H^5,H. The latter is also obtained when iodide of ethyl is decomposed, in presence of water, either by the action of light or by zinc (*vid.* p. 171; also *Chem. Soc. Qu. J.* 3, 338).

Methyl does not combine directly with any of the elementary bodies. According to the radical-theory, however, it is *capable* of entering into combination with nearly all of them. Thus, *Methyl-ether*, $\frac{C^2H^3}{C^2H^3}O^2$, is its oxide (p. 191); *Wood-spirit*, $\frac{C^2H^3}{H}O^2$, its hydrated oxide. With Sulphur it forms corresponding compounds. With Iodine, Bromine, Chlorine, Fluorine, and Cyanogen, it forms ethers of the second class (p. 190). With Nitrogen, it forms *Trimethylamine* and *Tetramethylium;* with Nitrogen and Hydrogen, *Methylamine* and *Dimethylamine.* With Zinc it forms a compound radical called *Zinc-methyl*, C^2H^3Zn; with Antimony, *Stibmethyl*, $(C^2H^3)^3Sb$, and *Stibmethylium*, $(C^2H^3)^4Sb$. It may also be considered as existing in *Cacodyl*, C^4H^6,As=$(C^2H^3)^2$As, and in P. Thénards phosphorus-base, $C^3H^9P=(C^2H^3)^3P$. It exists also in conjunction with other organic radicals, in many other compound ammonias, *e. g., Methylethylamine, Methylaniline,* &c. &c. ¶

Marsh-gas. $C^2H^4 = C^2H^3,H$.

VOLTA. *Ueber die entzündbare Luft der Sümpfe,* übers v. Köstlin, Strasburg, 1778.

CRUIKSHANK. *Nichols. J.* 5, 1; also *Scher. J.* 7, 371; also *Gilb.* 9, 103.

DEIMAN, PÄTS VAN TROOSTWYK, LAUWERENBURGH & VROLIK. *Gilb.* 2, 201; also *Crell, Ann.* 1795, 2, 195 and 310.—BERTHOLLET. *Mém. de l'Académie des Sc.* 1785.—*Mém. de l'Institut.* 4, 269; also *Scher. J.* 10, 575.—*Mém. d'Arcueil,* 2, 68 and 484; also *Gilb.* 34, 390.

TH. SAUSSURE.—The gas obtained from Alcohol and Ether at a red heat. *J. Phys.* 64; also *Gilb.* 129, 287.

W. HENRY.—Gas obtained by dry distillation. *Nicholson, J.* 1805; also *Gilb.* 22, 58.—Electrization by the gas produced from coal. *Phil. Trans.* 1808 and 1809; abstr. Gilb. 36, 298.—*Phil. Trans.* 1821, 136; also *N. Tr.* 6, 2, 225.

TH. THOMSON.—Gas obtained by the dry distillation of Peat. *Nicholson J.* 1807; also *Gilb.* 34, 417.

BERZELIUS. *Gilb.* 37, 466.

DALTON. *System of Chemistry*, 2, 255.

BRANDE.—Coal-gas. *Phil. Trans.* 1820, 11; also *Ann. Chim. Phys.* 16, 66; abstr. *N. Tr.* 6, 2, 218.

DUMAS. *Ann. Chim. Phys.* 73, 92; also *Ann. Pharm.* 33, 187; also *J. pr. Chem.* 19, 310.

G. BISCHOF.—Pit-gas. *N. Ed. Phil. J.* 28, 183; 29, 309.

GRAHAM.—Pit-gas. *Phil. Mag. J.* 28, 437.

SYN. *Light Carburetted Hydrogen, Protocarburetted Hydrogen, Marsh-air, Pit-gas; Heavy Inflammable Air, Heavy Combustible Air; Schwere brennbare Luft, Sumpfgas, Sumpfluft, Grubengas; Gas des marais; Gas hydrogène carburé, Gas hydrogène protocarboné* [Leforme]: — First examined by Volta in 1778, in the form of marsh air; also by Priestley, Cruikshank, Dalton, W. Henry, and others.

Sources. 1. In the mud of bogs, as *Marsh-air* (*Sumpfluft*). It is formed there by the putrefaction of organic substances, such as woody fibre; and rises, when the mud is stirred, together with a large quantity of carbonic gas and a small quantity of nitrogen. It does not contain carbonic oxide. (W. Henry.)

2. In coal-mines, as *Mine-gas or Pit-gas*, where it mixes with the air of the mine and forms an explosive mixture, which on the approach of a lamp, if not surrounded with Davy's wire-gauze (II. 34, 35), causes terrible explosions; *Fire-damp* (*Feurige Schwaden, Schlagende Wetter, Feu terrou ou grisou*). In these mines, the gas appears to be produced, not by the action of strong heat upon the coal—inasmuch as it is free from carbonic oxide and generally also from olefiant gas—but rather by a decomposition of the coal induced by the presence of water. According to W. Henry, it arises from the decomposition of water by carbon as follows:

$$4C + 4HO = 2CO^2 + C^2H^4.$$

Pit-gas rarely contains any other combustible gas, but is generally mixed with air, sometimes containing excess of nitrogen, and sometimes also with carbonic acid.—According to Turner (*Phil. Mag. J.* 14, 1), the following gaseous mixtures are found in the coal-mines at Newcastle:

	Sp. gr.	Marsh-gas.	Air.	Excess of Nitrogen.	Carbonic acid.
Bentham Coal Seam	0·6024	91	9		
Yard Coal Seam	0·6000	93	7		
High Main Seam	0·6196	85	8	7	
Low Main Seam	0·8228	37	46·5	16·5	
Hutton Seam	0·9660	7	82	11	
Adelaide Pit Hutton Seam	0·8660	28	67·5	4·5	
Eppleton Jone Pit Hutton Seam	0·7470	50	6	44	
Blosson Pit Hutton Seam	0·7800	50	23	27	
Bensham Coal Seam	0·6391	81·5	18·5		
Jarrow Colliery Seam	0·6209	89	11		
Bentham Seam	0·7278	68	28·7		3·3

Graham (*Phil. Mag. J.* 28, 437) found the following:

	Sp. gr.	Marsh-gas.	Nitrogen.	Oxygen.
Five-quarter Seam, Gateshead Colliery	0·5802	94·2	4·5	1·3
Bensham Seam, Hebburn Colliery	0·6327	....	....	0·6
Killingworth Colliery	0·6306	82·5	16·5	1·0

These three gases are perfectly free from olefiant gas, hydrogen, carbonic oxide and carbonic acid. For: 100 vol. mixed with 100 vol. chlorine, placed in the dark for 18 hours, and then washed with potash-ley, take up only 5 vol.; and the pure marsh-gas prepared from acetates takes up quite as much when similarly treated. Phosphorus does not burn in a gaseous mixture which contains but $\frac{1}{100}$ of olefiant gas or of the vapour of any other hydrocarbon; but in the above-mentioned pit-gases it continues to shine brightly; hence they must be free from these hydrocarbons. —Platinum-black does not alter the volume of the three gases in 24 hours, and produces neither water nor carbonic acid; but on the addition of 1 per cent. of hydrogen, condensation begins even in three minutes; and if 1 per cent. of carbonic oxide be added, the gas will render lime-water turbid in the course of half an hour. Potassium fused in pit-gas does not become covered with the green, fusible substance which carbonic oxide forms with it, but merely produces the trifling expansion that it would produce in the gas obtained from acetates, probably due to separation of hydrogen. (Graham.)

The pit-gas which escapes from fissures in the oldest coal-formation in the Saarbrück, contains, according to Bischof, neither oxygen, carbonic oxide, nor vapour of oily hydrocarbons condensable by oil of vitriol; but small quantities of olefiant gas, and likewise the following:

	Sp. gr.	Marsh-gas.	Olefiant gas.		Carbonic acid.
Wellesweiler Pit	0·5742	87·43	6·05	2·22	4·30
Gerhard's Pit	0·6513	79·84	1·90	14·36	3·90

The presence of olefiant gas is indicated by Bischof's experiments with chlorine and oxygen, but not by those made with oxide of copper. According to Bischof, also, the pit-gas is produced, not by fire but by putrefaction; and the nitrogen contained in it proceeds, not from the air, but from putrefied nitrogenous matter. From the bore-hole of an Artesian well at Liekweg in the Schaumburg, which penetrates into the new coal-formation of the lias, there issues, probably from the highly carboniferous shale, a gas which burns with a bluish flame, yellow at the apex, and, after being freed from carbonic acid, is found to contain 79·10 per cent. of marsh-gas, 16·11 olefiant gas, and 4·79 of an incombustible gas, probably nitrogen, but neither carbonic oxide, nor any vapour condensable by oil of vitriol. (Bischof.)

3. Marsh-gas likewise issues from the earth in places more or less removed from coal-strata. From the argillaceous banks of a stream at Bedlay, 7 English miles from Glasgow, and at least three from the coal-formation, there issues a mixture of 87·5 vol. marsh-gas and 12·5 air, which, if set on fire, continues to burn with a yellow flame for five weeks; the gas issues in largest quantity and with greatest force from the stream itself. (Th. Thomson, *N. Ed. Phil. J.* 1, 67.)—The gas which maintains the *Sacred Fire of Baku*, is marsh-gas, mixed with 6 per cent. of nitrogen, and from 1 to 5 per cent. of carbonic acid, also with vapour of rock-oil; hence the gas, when analyzed by means of oxide of copper ignited in a tube, yields too much carbon (77·5C and 22·5H). (Hess, *J. pr. Chem.* 13, 514.)—¶ A remarkable evolution of gas from the

earth has been observed at the village of Charlemont, in Staffordshire; a workman was led to the discovery of it by the absence of all vegetation near the spot. By fixing tubes in the ground, he obtained a constant stream of gas, which burned with a clear pale bluish flame, giving both light and heat. He likewise found a similar issue of gas at his cottage, 150 yards distant from the place where he first observed it; and the supply was so abundant, that no perceptible diminution took place, even after the gas had been burnt for several weeks from nine tubes. The spot is more than a mile from any coal-mine; but many disused fissures occur in the same locality, and the gas probably finds its way through these from the large coal-strata in the neighbourhood. 1000 volumes of the gas were found to contain 996 marsh-gas, 3 carbonic acid, and 1 hydrogen or nitrogen. Sp. gr. 0·56126. It contains therefore less carbonic acid and nitrogen than the gas which issues from bogs, or that which is found in old mines. (S. S. Howard, *Chem. Gaz.* 1849, 409; *Inst.* 1849, 406; *Jahresber. L. & K.* 1849, 789.) ¶

Formation. 1. By the putrefaction of certain organic substances.

2. By the dry distillation of such substances, or by passing their vapours through a red-hot tube; *e. g.*, wood, turf, coal, resin, fat, alcohol, ether, camphor. The gas thus obtained is a mixture, in very variable proportions, of hydrogen, carbonic oxide, marsh-gas, and olefiant gas, together with the vapours of empyreumatic oils and camphors.—Gaseous mixtures of this nature were regarded by Saussure (*Gilb.* 29, 287), Berthollet (*Gilb.* 34, 390), Thomson (*Gilb.* 34, 417), and Murray (in his *System of Chemistry*), as peculiar simple gases, which they designated by the common name of *Oxycarburetted Hydrogen Gas.* On the contrary, Cruikshank, W. Henry (*Ann. Phil.* 15, 37), Dalton (*System*, 2, 260), and H. Davy (*Elements*, 1, 283), adopted the simpler hypothesis, more consistent with the doctrine of definite proportions, that these so-called oxycarburetted hydrogen gases are mixtures of carbonic oxide, which yields the oxygen, with hydrogen and various hydrocarbons; any required oxycarburetted hydrogen gas may, indeed, be obtained by mixing carbonic oxide with the last-mentioned gases. The mixtures may be freed from olefiant gas by chlorine in the dark, or by iodine; the residual gas, consisting of hydrogen, carbonic oxide, and marsh-gas, exploded with excess of oxygen; the diminution of volume ascertained by measurement, and the quantity of carbonic acid by absorption with caustic potash; and the proportion of the three gases in the mixture, then determined by calculation. A measured volume, *e. g.*, 100 vol. of such a mixture of carbonic oxide, hydrogen, and marsh-gas, is mixed with a measured quantity of oxygen, more than sufficient for the complete combustion of the gas, and the mixture exploded by the electric spark. The residual gas is measured; hydrate of potash then introduced into it; and when the absorption is complete, the residual gas is also measured. This residue, deducted from the volume of oxygen introduced, gives the quantity of oxygen (=O) consumed in the combustion. The decrease of bulk caused by the potash gives the volume of carbonic acid produced (=C). From these data, we may calculate (the quantity of combustible gas being made = 100 vol.), first, the hydrogen = 100−C; then the marsh-gas $= \frac{2O-100}{3}$; and, lastly, the carbonic oxide, = C *minus* the marsh-gas.—

If the gaseous mixture analyzed also contains nitrogen, the proportion of the oxygen to the nitrogen in the residue left after the action of the potash must first be determined eudiometrically, and the quantity of

nitrogen thus found deducted from the gaseous mixture, and reckoned with the oxygen consumed. For further details, *vid.* Sylvester (*Ann. Phil.* 2, 215; also *Schw.* 33, 234), and particularly, Bischof (*Schw.* 37, 133); also Regnault (*Cours élémentaire de Chimie.* Paris, 2me Ed. pp. 73—103).

3. By heating acetic acid or acetone with excess of a fixed alkali, the heat being kept below redness. (Persoz, *Revue scientif.* 1, 51; Dumas, *Ann. Chim. Phys.* 73, 92.) For acetic acid:

$$C^4H^4O^4 = C^2O^4 + C^2H^4;$$

for acetone, in which case the water of the hydrate of potash takes part in the action:

$$C^6H^6O^2 + 2HO = C^2O^4 + 2C^2H^4.$$

The carbonic acid produced remains in combination with the alkali.

Alcohol-vapour passed through a nearly red-hot tube filled with baryta, is resolved into carbonic acid, which unites with the baryta, and a kind of marsh-gas—which has the same density as ordinary marsh-gas, requires the same quantity of oxygen to burn it, and produces the same quantity of carbonic acid by its combustion; but nevertheless exhibits a totally different reaction with bromine (p. 256). (Pelouze & Millon, *Ann. Pharm.* 33, 185.) The gas obtained by this process is not pure marsh-gas, but a mixture of that compound with olefiant gas and hydrogen, perhaps also with carbonic oxid. (Dumas & Stas, *Compt. rend.* 10, 260; also *J. pr. Chem.* 20, 314.)

Whether the gas evolved during the solution of cast-iron in dilute sulphuric or hydrochloric acid is marsh-gas, as sometimes supposed, or merely hydrogen charged with the vapour of an oily hydrocarbon, is a point not yet decided (*comp.* V., 216, 217).

Preparation. A mixture of 2 pts. of crystallized acetate of soda, 2 pts. hydrate of potash, and 3 pts. lime, is heated in a retort. (Dumas.) The lime preserves the retort from corrosion by the hydrate of potash. This method yields the purest gas.—Persoz passes the vapour of acetone slowly through a U-shaped tube of glass or iron, in which hydrate of potash is heated to fusion; the gas thus produced contains a small quantity of carbonic acid.

2. By stirring the mud of a stagnant pool; collecting the gas, as it bubbles up, in inverted bottles filled with water, and having funnels inserted into their mouths; and agitating it with milk of lime to remove carbonic acid and any sulphuretted hydrogen that may be present.—The marsh-gas thus obtained contains for 100 vol. of pure gas, 7 vol. nitrogen, according to W. Henry, and 28 vol. nitrogen, according to Saussure. These 128 vol. (100 marsh-gas + 28 nitrogen) exploded with excess of oxygen, consume, not 200 but 224 vol. oxygen, and produce, not 100 but 103 vol. carbonic acid gas, perhaps because the nitrogen belongs essentially to the compound. (Th. Saussure, *Mém. de Genève*, 8, 184.)

3. The gaseous mixture obtained by the dry distillation of wood, peat, or coal, or by passing alcohol-vapour through a red-hot tube, is freed from carbonic and hydrosulphuric acid by milk of lime, then from olefiant gas by the action of chlorine in the dark, and, lastly, from the excess of chlorine by again treating it with milk of lime.—After this treatment the marsh-gas is merely contaminated with hydrogen and carbonic oxide. According to Bischof, the latter cannot be removed by heated potassium, because the marsh-gas appears to be likewise decomposed during the

heating.—W. Henry (*Ann. Phil.* 25, 428) washes coal-gas with chlorine-water, and with potash to remove the excess of chlorine; then mixes it with 1½ vol. oxygen, and passes it into a retort containing spongy platinum heated to 177°, at which temperature all the hydrogen and carbonic oxide burn away, but none of the marsh-gas. He then removes the resulting carbonic acid by potash, and the excess of oxygen by means of a suitable reagent. Marsh-gas then remains, contaminated only with a small quantity of nitrogen. Iodine likewise serves to purify coal-gas from all other kinds of carburetted hydrogen-gas, with some of which it forms liquid, with others solid compounds; whereas, in marsh-gas, it remains unaltered and preserves its lustre. (Graham, *Chemie*, 2, 103.)

Properties. Colourless gas. Refracting power (I., 95).—Density = 0·5576 (Thomson), 0·6 (Dalton), 0·6—0·78 (W. Henry). Does not support the combustion of other bodies. Highly combustible. Neutral. According to some observers, it has a faint, unpleasant odour; but, according to Erdmenger & Krug v. Nidda, also according to Bischof and Graham, it is inodorous. Tasteless. When inhaled, it is only negatively deleterious, like hydrogen (II., 45). Miners who often breathe an air containing $\frac{1}{11}$ of marsh-gas, do not lose their health from it; when they breathe a mixture still richer in marsh-gas, they feel a slight pressure on the forehead, temples, and eyes; but this effect soon goes off when they get into the open air. (Bischof.)

				Vol.	Density.
2C	12	75	C-vapour	2	0·8320
4H	4	25	H-gas	4	0·2772
C^2H^4	16	100	Marsh-gas	2	1·1092
				1	0·5546

Decompositions. 1. When electric discharges are repeatedly passed through this gas (Dalton), or when the polar platinum wires of a voltaic battery are brought to a state of ignition within it, or when it is several times passed through a red-hot tube, it is converted, with deposition of charcoal, into pure hydrogen gas, which occupies twice the original volume. When 6200 electric sparks are passed, in the space of 30 hours, through perfectly dry pit-gas freed from carbonic acid, only ⅓ of the marsh-gas is decomposed, although the gas ceases to expand long before the passage of the sparks is terminated. The charcoal separated in this decomposition has a strong odour of turpentine. The complete decomposition which Dalton obtained was perhaps due to the presence of moisture in his gas. (Bischof.) Pit-gas is also but imperfectly decomposed by passing it repeatedly through a white-hot porcelain tube. The gas ceases to expand after it has been passed four times through the tube, and after the tenth passage, only ⅓ of the marsh-gas is decomposed. The gas, when thus treated, acquires an empyreumatic odour. If, after passing through the ignited tube, it be conducted into a Liebig's bulb-apparatus filled with oil of vitriol, yellow drops condense in the tube of the apparatus, and flow into the oil of vitriol. This liquid gradually acquires a dark brown colour and strong empyreumatic odour, and becomes covered in the first bulb with greenish drops, which, on cooling, partly solidify in greenish masses. The oil of vitriol, on being diluted with water, yields an inconsiderable precipitate, and is converted into a light brown, sweet-smelling liquid. If the bulb contains alcohol instead of oil of vitriol, the tube of the apparatus becomes filled with fumes, which condense in brownish yellow drops, and impart to the alcohol a

continually deepening wine-yellow colour, and an odour like that of turpentine; in the glass tube which is connected by a stopper with the porcelain tube, a white sublimate collects, coloured by a brown liquid. The alcohol appears to absorb all these empyreumatic products. It appears then that, in addition to charcoal and hydrogen, various empyreumatic products are eliminated. The charcoal deposited in the porcelain tube is brownish yellow at the entrance of the tube, which is comparatively cool, but in the hotter part it is deposited in strongly lustrous graphitic laminæ, which roll up into tubes an inch long. The graphite found in the fissures of Plutonic rocks has perhaps been formed in a similar manner, by the passage of marsh-gas [or some other hydrocarbon] while the rock was still in a state of ignition.

2. The gas, when set on fire in the air, burns with a moderately bright flame, yellow above and bluish below: 2 vol. marsh-gas mixed with 4 or more volumes of oxygen, and exploded in the detonating tube by the electric spark, consume 4 vol. oxygen, and form 2 vol. carbonic acid gas. (Dalton, W. Henry, H. Davy, Dumas.) The 2 vol. C-vapour with 2 vol. O-gas form 2 vol. CO^2-gas; and the 4 vol. H with 2 vol. O form water. When 2 vol. marsh-gas are exploded with only 2 vol. oxygen, 2 vol. carbonic oxide and 2 vol. hydrogen are produced, without any change of volume. (Dalton.) In this case, 2 vol C-vapour with 1 vol. O form 2 vol. CO; and of the 4 vol. H, 2 volumes unite with 1 vol. O, and form water, the other 2 volumes remaining unaltered. According to Dalton, a small quantity of carbonic acid is occasionally produced at the same time. Since 1 vol. marsh-gas requires 2 vol. oxygen to burn it completely, it likewise requires 9·53 vol. of common air (21 : 100=2 : 9·53). A mixture of 1 vol. marsh-gas and 7 or 8 vol. air may be ignited even by a small electric spark, and detonates more strongly than any other mixture of the same gas with air; but not so strongly as ordinary detonating gas. As the proportions deviate from that of 1 : 7, the explosion becomes weaker, and requires a stronger electric spark to induce it; and when the excess of either gas reaches a certain limit, the mixture is no longer explosive. A mixture of 1 vol. marsh-gas and 15 vol. air is not set on fire by the electric spark, but enlarges the flame of a candle held within it; a mixture of 1 vol. marsh-gas and 2 vol. air burns without noise. (H. Davy.) The explosion is strongest with a seven-fold measure of air, and is then accompanied with a yellow flame; when the quantity of air is larger, a pale blue flame passes slowly through the mixture; with 20 volumes of air, the mixture will no longer take fire. (Turner.) 1 vol. pit-gas from the Wellesweiler pit (p. 250) detonates violently with 7 vol. air, but slowly and feebly with 16 volumes; when mixed with 6 or with 17 vol. air, it is not set on fire by the electric spark. (Bischof.) A mixture of marsh-gas with the proper quantity of air or oxygen gas may also be set on fire by flaming bodies, or by white-hot, sparkling iron, but not by iron at a red heat; it is therefore much less inflammable than hydrogen or carbonic oxide, and less also than olefiant gas. (H. Davy.) Neither is it inflamed by burning tinder, even though the tinder be strongly blown upon. (Bischof.)

Spongy platinum when cold does not set fire to a mixture of 1 vol. marsh-gas and 2 vol. oxygen (Döbereiner); but when heated above 190°, it induces slow combustion. (W. Henry.) If, however, detonating gas be added to the mixture, the platinum is thereby raised to a red heat, and then brings about the combustion of the marsh-gas itself. (Döbereiner.) A ball of platinum introduced into a mixture of 1 vol. detonating gas and from ½ to 10 vol. marsh-gas, condenses only the detonating

gas; it is only when the quantity of marsh-gas is reduced to less than ⅓ of the detonating gas that carbonic acid is produced; but on adding more oxygen to the mixture, carbonic acid is produced, if the quantity of detonating gas amount to more than four times that of the marsh-gas. (W. Henry.) In a mixture of marsh-gas, carbonic oxide, and oxygen, spongy platinum heated to 204° induces only slow combustion of the carbonic oxide; and in a mixture of marsh-gas, hydrogen, carbonic oxide, and oxygen, spongy platinum heated to 249° induces slow combustion only of the hydrogen and carbonic oxide. (W. Henry, *Ann. Phil.* 25, 418.) Oxidized sulphide of platinum (VI., 231) decomposes marsh-gas, with great evolution of heat. (Döbereiner.) A mixture of marsh-gas and oxygen is not altered by putrefying substances, which condense detonating gas (II., 5). (Saussure.)

3. A dry mixture of 2 vol. marsh-gas and 4 vol. chlorine remains unaltered in the dark, but detonates by the electric spark, with separation of charcoal and formation of somewhat more than 8 vol. hydrochloric acid gas. (H. Davy.) The same decomposition takes place in a few days if the mixture be merely exposed to light. (Gay-Lussac and Thénard.) The mixture, in whatever proportions it may be made, does not exhibit any immediate reaction on exposure to light; but on mixing 2 vol. marsh-gas (prepared from acetate of potash) with 6 vol. chlorine, a violent explosion, attended with destruction of the containing vessel, soon takes place, even in diffused daylight. (Dumas.) — Equal volumes of Wellesweiler pit-gas and chlorine exert no action upon each other, even in sunshine, but a mixture of 2 vol. chlorine with 1 vol. pit-gas exposed to sunshine over water, detonates very slightly, with deposition of charcoal. Sometimes the explosion takes place immediately, sometimes not even for several minutes, viz., when the chlorine-gas is contaminated with air. The explosion is more quickly produced by passing the marsh-gas, which is the lighter of the two, into the chlorine, than the contrary way, because in the former case, the gases mix more readily.—The explosion succeeds best in a cylinder 1½ inch wide, 18 inches high, and filled to the height of 10 inches with the mixture. On exposing the vessel to sunshine, the water surrounding the bottom sinks at first; then white fumes are produced, and charcoal is deposited. The charcoal has a sharp taste like that of mustard, and the cylinder smells of oil of olefiant gas.—If the sun is but slightly obscured by a cloud, white fumes are produced and the water rises, but no charcoal is deposited; neither does any explosion take place, even if the sun become clear again during the experiment. When the whole of the chlorine has been absorbed by the water, the vessel being exposed to the sun, the contents smell strongly of oil of turpentine. (Bischof.)

If the explosion be prevented by mixing the marsh-gas with an equal volume of carbonic acid, chlorine added in excess gradually forms hydrochloric acid gas and an oily liquid consisting of a small quantity of chloroform, C^2HCl^3, and a large quantity of bichloride of carbon, C^2Cl^4 (Dumas):

$$C^2H^4 + 8Cl = C^2Cl^4 + 4HCl;$$

the chloroform must be regarded as a transition-product.—Melsens (*Ann. Chim. Phys.* 74, 110; *Ann. Pharm.* 35, 353; also *J. pr. Chem.* 21, 266) obtained the same chloride of carbon, C^2Cl^4 (accompanied, however, with a very small quantity of stellate crystals), with light carburetted hydrogen obtained from marshes,—a proof that this last-mentioned gas is identical

with that prepared from the acetates.—Marsh-gas is not altered by passing through heated chloride of sulphur, pentachloride of phosphorus, or pentachloride of antimony. (Dumas.)

In presence of moisture, and in the light, but not in the dark, marsh-gas is slowly decomposed by chlorine, yielding hydrochloric acid and carbonic acid or carbonic oxide. (W. Henry.)—When at least 8 vol. chlorine are mixed with 2 vol. marsh-gas, 2 At. (or 2 vol.) carbonic acid and 8 At. (or 16 vol.) hydrochloric acid are produced :

$$C^2H^4 + 8Cl + 4HO = 2CO^2 + 8HCl.$$

With 6 vol. chlorine, the products are 2 At. (or 2 vol.) carbonic oxide and 6 At. (or 12 vol.) hydrochloric acid :

$$C^2H^4 + 6Cl + 2HO = 2CO + 6HCl.$$

Since this decomposition does not take place in the dark, a mixture of marsh-gas and olefiant gas may be freed from the latter by adding chlorine and placing the mixture in the dark ; the olefiant gas will then be condensed in the form of Dutch liquid, and the excess of chlorine may be removed from the marsh-gas by potash. (W. Henry.)—When 2 volumes of Wellesweiler pit-gas are mixed with only 4 vol. chlorine, and the mixture left over water for 5 hours in daylight, there remains, after absorption of carbonic acid by potash, 1 vol. of light carburetted hydrogen which burns with a whitish blue flame. (Bischof.) [Is there no carbonic oxide formed in this case ?]

Bromine exerts but a very slow decomposing action in daylight on the carburetted hydrogen of marshes, but acts somewhat differently on the gas obtained from acetate of potash. The gas obtained from alcohol by heated baryta (fourth mode of formation), is decomposed by bromine with the greatest violence, yielding hydrobromic acid and the same ethereal liquid, C^4H^4,Br^2, that is obtained by bringing olefiant gas in contact with bromine. There are, therefore, three isomeric varieties of C^2H^4 to be distinguished. (Pelouze and Millon, *Ann. Pharm.* 33, 185.)—But, according to Dumas and Stas (*Compt. rend.* 10, 260 ; also *J. pr. Chem.* 20, 316), the gas obtained from alcohol and baryta is a mixture of marsh-gas, olefiant gas, hydrogen, and probably also carbonic oxide.

A mixture of marsh-gas and nitric oxide is not inflamed by the electric spark.

4. Oil of vitriol does not absorb marsh-gas ; but anhydrous sulphuric acid decomposes it, with formation of water and sulphurous acid and deposition of charcoal. (Aimé, *J. Pharm.* 21, 86 ; also *J. pr. Chem.* 6, 79.)

Combinations. Water absorbs $\frac{1}{17}$ of its volume of marsh-gas. (Dalton.) —Certain organic liquids likewise absorb it in small quantity.

Methylic Ether or Methyl-ether. $C^2H^3O = C^2H^2,HO$.

Discovered by Dumas and Péligot (*Ann. Chim. Phys.* 58, 19).—*Oxide of Methyl, Wood-ether ;—Holzäther, Methylenäther, Methyloxyd,* (Berz.) ;—*Oxyde de Methyle, Hydrate de Methylène.* (Dumas and Péligot.) [Nalaforme.]

Formation. By heating wood-spirit, $C^2H^4O^2$, with oil of vitriol (Dum. Pél.), or with excess of pulverized anhydrous borax (Ebelmen, *N. Ann. Chim. Phys.* 16, 138).

Preparation. 1 pt. of wood-spirit is heated with 4 pts. oil of vitriol, and the resulting methyl-ether gas placed in contact with caustic potash for several hours to free it from carbonic and sulphurous acid.—Sometimes the gas is contaminated with vapour of sulphate of methyl, which gives it a garlic odour. (Dumas, Péligot.)—Kane (*Ann. Pharm.* 19, 166) passes the gas evolved, by heating equal measures of wood-spirit and oil of vitriol, through milk of lime, and then into water freed from air by boiling, which absorbs the gas abundantly. From this solution he evolves it in a state of purity by gentle heating, and dries it by passing it through a tube containing chloride of calcium.

Properties. Colourless gas, which does not liquefy at −15°. Sp. gr. 1·617. Neutral towards vegetable colours. Of ethereal odour.

According to Dumas & Peligot.

2C	12	....	52·18
3H	3	....	13·04
1O	8	....	34·78
C^2H^3O	23	....	100·00

	Vol.		Density.	Or:	Vol.		Density.
C-vapour	2	....	0·8320	C^2H^2-gas	2	....	0·9706
H-gas	3	....	0·2079	Vapour of water	1	....	0·6239
O-gas	½	....	0·5546				
Methyl-ether gas	1	....	1·5945	Methyl-ether gas	1	....	1·5945

C^2H^2,HO (*Th.* 1) = C^2HO,H^2 (*Th.* 2) = C^2H^3,O (*Rad.*) $[= \left.\begin{matrix}CH^3\\CH^3\end{matrix}\right\} O$.—(Williamson; Gerhardt; Chancel.)] According to the radical-theory, it is supposed to contain the radical *Methyl* = C^2H^3.—It is polymeric with alcohol, $C^4H^6O^2$, and has the same vapour-density as the latter.

Decompositions. Methyl-ether gas, when set on fire in the air, burns with a flame like that of alcohol. (It is blue, and gives scarcely any light. *Kane.*)—1 volume of the gas consumes in the detonating tube 3 vol. oxygen, and forms 2 vol. carbonic acid gas (Dumas & Péligot); 2 vol. oxygen gas convert the 2 vol. carbon-vapour into 2 vol. carbonic acid; 1 vol. oxygen gas, together with the ½ vol. already contained in the ether, converts the 3 vol. hydrogen into water.

2. Methyl-ether gas mixed perfectly dry with chlorine first forms white fumes of hydrochloric acid, and, after a few minutes, explodes and bursts the apparatus. (Malaguti, *Ann. Chim. Phys.* 70, 379.) If the explosion be prevented by causing the two gases to come together in a large globe from two tubes at some distance from each other, they form hydrochloric acid, and condense into a liquid, C^2H^3ClO, which, by the further action of chlorine, is first converted into C^2HCl^2O, and afterwards, in sunshine, into C^2Cl^3O. (Regnault, *Ann. Chim. Phys.* 71, 396.)—Methyl-ether gas is not perceptibly altered by passing through chlorosulphuric acid, $SClO^2$. (Regnault.)

3. Methyl-ether gas, passed through heated potash-lime, yields free hydrogen and formiate of potash, which, by a stronger heat, is converted into carbonate (Dumas & Stas, *Ann. Chim. Phys.* 73, 157):

$$C^2H^3O + KO + 2HO = C^2HKO^4 + H^4.$$

Combinations. Water at 18° absorbs 37 volumes of methyl-ether gas, thereby acquiring an ethereal odour and peppery taste. (Dum. Pel.). The water acquires a pleasant aromatic taste and smell, and gives off

the gas when gently heated. (Kane.)—Oil of vitriol absorbs the gas more abundantly than water, and gives it off partially on being diluted with water.

Wood-spirit and alcohol likewise absorb the gas much more abundantly than water. (Dumas & Peligot.)

Wood-spirit, Methylic Alcohol, or Methyl-alcohol.

$C^2H^4O^2 = C^2H^3,H^2O^2$.

Colin. *Ann. Chim. Phys.* 12, 206.—Döbereiner. *Schw.* 32, 487.—Macaire & Marcet, Jun. *Bibl. univ.* 24, 126; also *Schw.* 40, 348.—Reichenbach. *Schw.* 69, 241.

Liebig. *Ann. Pharm.* 10, 315.

Dumas & Péligot. *Ann. Chim. Phys.* 58, 5; also *Ann. Pharm.* 15, 1; also *J. pr. Chem.* 3, 369.—*Ann. Chim. Phys.* 61, 193; also *J. pr. Chem.* 8, 58.

Kane. *Phil. Mag. J.* 10, 45 and 116; also *Ann. Pharm.* 19, 164.

Weidmann & Schweizer. *Pogg.* 43, 593.—*J. pr. Chem.* 23, 3.

Kuhlmann. *Ann. Pharm.* 33, 208.

Syn. *Pyroxylic Spirit, Wood-naphtha, Hydrated Oxide of Methyl; —Holzgeist, brenzlicher Holzgeist, brenzlicher Holzessiggeist, Methyloxyd-Hydrat; —Esprit de bois, Esprit pyroxylique, Bihydrate de Methylene* (Dum. & Pel.) *Hydrate d'oxide de méthyle.* [Neleforme.]

Taylor (*Tilloch's Phil. Mag.* 60, 315) in 1812, first observed in *Wood-vinegar*, the watery liquid obtained in the dry distillation of wood, an alcoholic liquid which he regarded as the ether of wood-vinegar; Colin, in 1819, declared this liquid to be acetone; Döbereiner, in 1821, pronounced it to be alcohol. Macaire & Marcet, who however examined a specimen contaminated with a large quantity of empyreumatic oil, declared it to be a compound *sui generis;* Reichenbach took it for a mixture of alcohol and acetone. Ultimately it was discovered that wood-vinegar contains at least three peculiar spirituous liquids, viz., *Wood-spirit*, which was first accurately characterized and subjected to a detailed investigation by Dumas & Péligot in 1835;—*Lignone*, examined by Gm., Liebig, and Weidmann & Schweizer;—and *Acetone*, a compound previously known.

According to Dumas & Péligot, the proportion of methylic alcohol in wood-vinegar amounts to about 1 per cent.; but the quantity varies, many samples of wood-vinegar consisting principally of methylic alcohol, others chiefly of lignone.—Wood-spirit is evolved in especial abundance when substances consisting of woody fibre are mixed with an equal weight of hydrate of potash and a smaller quantity of water, and gradually heated to the boiling-point of mercury. (Péligot, *Ann. Chim. Phys.* 73, 218.)

Preparation. In the dry distillation of wood there is obtained a tarry matter called *Wood-tar*, and a watery liquid called *Wood-vinegar* or *Pyroligneous acid*. This liquid is a mixture of water, acetic acid, acetate of ammonia, wood-spirit, lignone, acetone, acetate of methyl (Reichenbach's *Mesite*), aldehyde, the compound called *Mesite* by Weidmann & Schweizer, empyreumatic oils, pyroxanthine, and small quantities of other substances. By distilling about 10 or 15 per cent. from this wood-vinegar, we obtain *crude Wood-spirit*, which consists chiefly of the more volatile matters, viz., acetic acid, ammonia, methylic alcohol, acetate of methyl, lignone, acetone, aldehyde, mesite, pyroxanthine, and volatile empyreumatic oils.

1. The wood-vinegar poured off from the tar is distilled till $\frac{1}{10}$ has passed over; this $\frac{1}{10}$ is repeatedly rectified over slaked lime, the watery portion being each time left behind; and the rectified product is mixed with sulphuric acid, to precipitate tar and fix the ammonia which has been set free. The resulting liquid is then again repeatedly distilled over slaked lime, till it mixes with water without turbidity, no longer turns brown in the air, or exerts any action on vegetable colours, or gives a black precipitate with mercurous nitrate. It is then freed from the still remaining water by a second distillation with an equal quantity of pounded quicklime, a small quantity of mercury being added to prevent percussive ebullition. All these distillations must be performed in the water-bath. (Dumas & Péligot.)—Wood-spirit cannot be dehydrated by chloride of calcium, because that substance retains it with great force (Dum. Pel.)

2. The empyreumatic oils are not completely removed by these distillations over lime, nor even by distillation over potash or sulphuric acid. Hence the crude wood-spirit must be saturated with chloride of calcium and distilled in the water-bath as long as any excess of methyl-alcohol passes over with the empyreumatic oil, lignone, acetone, &c. The residue mixed with water and again heated in the water-bath, gives off methyl-alcohol perfectly free from oil, and the distillate may be dehydrated by two distillations over quicklime. (Kane.)

Crude wood-spirit contains water, methyl-alcohol, acetate of methyl, lignone, and the mesite of Weidmann & Schweizer. In the first distillations with lime, methyl-alcohol is likewise separated from the acetate of methyl. When the distillate has thus been freed from empyreumatic oil, it may still contain, in addition to the methyl-alcohol,—lignone, Weidmann & Schweizer's mesite, together with a small quantity of empyreumatic oil (*Dumasin*). It is therefore saturated with chloride of calcium, and the solution distilled in the water-bath without further addition of chloride of calcium (which would also retain lignone). By this treatment the lignone and the mesite are made to pass over, together with a small quantity of methyl-alcohol; but a certain portion of empyreumatic oil remains behind with the compound of chloride of calcium and wood-spirit. Hence, on mixing this residue with water and distilling, pure methyl-alcohol passes over at first, requiring merely to be dehydrated with quicklime; but the subsequent portions of the distillate become continually richer in empyreumatic oil. (Weidmann & Schweizer, *J. pr. Chem.* 23, 4. *Comp.* Völckel, *Pogg.* 83, 272, 577; *Chem. Gaz.* 1852, 101.)

Properties. Transparent, colourless, mobile liquid. Sp. gr. 0·798 at 20° (Dum. Pel.); 0·7938 at 25° (Kopp, *Ann. Pharm.* 55, 195); 0·81796 at 0° (Kopp, *Pogg.* 72, 1; *Jahresber.* 1847–8, 65); 0·8207 at 0° (Pierre, *N. Ann. Chim. Phys.* 15, 325; *Jahresber.* 1847–8, 61).—Boils, under a pressure of 0·761 met. at 66·5° (Dum. Pel.); under a pressure of 0·744 met. at 60° (Kane); under a pressure of 0·7521 met. in contact with platinum wire, at 66°, with recently ignited charcoal bound round with platinum wire, at 65·5° (Kopp); under a pressure of 0·759 met. at 66 3° (Pierre); at 66·5° (Persoz).—Wood-spirit exhibits percussive ebullition, both when distilled alone and with lime, even in the water-bath (Dum. Pel.); with platinum wire it boils pretty quietly (Kopp); with mercury it boils quietly (Dum. Pel., Mitscherlich).—Vapour-density, 1·120 (Dum. Pel.); 1·1210 (Kane).—Has a peculiar aromatic odour, resembling that of alcohol and acetic ether. (Dum. Pel.)

		Dumas & Péligot.	Kane.	Weidmann & Schweizer.	Kopp.
2C	12	37·50	37·7	37·66	37·46	37·48
4H	4	12·50	12·4	12·39	12·80	12·66
2O	16	50·00	49·9	49·95	49·74	49·86
$C^2H^4O^2$	32	100·00	100·0	100·00	100·00	100·00

	Vol.	Density.	Or:	Vol.	Density.
C-vapour	2	0·8320			
H-gas	4	0·2772	Methylene-gas	2	0·9706
O-gas	1	1·1093	Aqueous vapour	2	1·2479
Methyl-alcohol vapour	2	2·2185		2	2·2185
	1	1·1092		1	1·1092

C^2H^2,H^2O^2 (*Th.* 1) = C^2HO,H^2O (*Th.* 2) = $C^2H^3O + HO$ (Rad.) = $\left.\begin{matrix}CH^3\\H\end{matrix}\right\}O$. (Williamson; Gerhardt; Chancel; *vid.* p. 17.)

Decompositions. In the circuit of the voltaic battery, anhydrous wood-spirit gives off no gas at the positive, but pure hydrogen at the negative pole; if it be then evaporated with addition of a little water, it deposits a small quantity of white matter, diffuses a peculiar odour, and finally leaves a yellowish-white resinous mass. Hence, the so-called anhydrous wood-spirit contains water of hydration, the hydrogen of which is set free, while its oxygen remains behind and converts part of the wood-spirit into resin.—If the wood-spirit contains hydrate of potash in solution, the evolution of gas is much quicker, and is produced even by batteries of a few pairs, which exert no action on pure wood-spirit. This influence is perceptible even when the quantity of potash-hydrate amounts to only $\frac{1}{10.000}$ part; and the increased evolution of hydrogen thereby produced far exceeds that which could be derived merely from the hydration-water in the hydrate of potash. The quantity of hydrogen evolved from wood-spirit containing $\frac{1}{100}$ pt. of potash-hydrate, is to that which is evolved in a voltameter containing acidulated water, and placed in the same circuit, as 10 : 12.—When the electric current is made to act for a quarter of an hour upon wood-spirit containing $\frac{1}{300}$ of potash-hydrate—in which time 1 cubic inch of hydrogen is evolved—the liquid is found to contain white flakes—exhibits, after evaporation with water, a sharp, aromatic taste, and leaves a small brown residue.—With larger quantities of potash-hydrate, carbonate of potash is likewise formed; a small quantity of gas is also evolved at the positive pole, being probably derived from the hydration-water of the potash. The liquid acquires a sharp taste, becomes turbid on the addition of water, and assumes a yellow colour, probably from separation of an oily or ethereal substance. (A. Connell, *Trans. Roy. Soc. Edinb.* vol. 4, 1837, March.)

2. Wood-spirit set on fire in the air burns with a flame like that of alcohol. (Dumas & Péligot.) The flame is pale blue, somewhat reddened at the apex, and gives less light than an alcohol-flame. (Gm.)—A small quantity of boracic acid is sufficient to colour the flame quite green, whereas the flame of alcohol to which a comparatively large quantity of the same acid has been added, merely acquires a green border. (Ebelmen, *N. Ann. Chim. Phys.* 16, 138.)—Wood-spirit, dropped on platinum-black, takes fire and burns, producing carbonic acid and water. (Dum. Pel.) Platinum-black prepared from platinate of soda by the action of

formic acid, sets fire to wood-spirit immediately; platinum-black obtained from the zinc-alloy sets fire to vapour of wood-spirit mixed with air. (Döbereiner, *Schw.* 66, 289; *Pogg.* 37, 548.)—Wood-spirit remains unaltered in vessels containing air; but when placed, together with platinum-black, under a receiver not exhausted of air, it is slowly converted, with evolution of heat, into formic acid (Dum. Pel.) :

$$C^2H^4O^2 + O^4 = C^2H^2O^4 + 2HO.$$

Spongy platinum moistened with wood-spirit does not act upon the air; but if moistened at the same time with strong caustic potash, it often becomes heated to redness, and converts the wood-spirit, first into formic acid, and afterwards into water and carbonic acid. (Döbereiner, *Ann. Pharm.* 53, 145.)

3. When dry chlorine gas is passed through wood-spirit, every bubble produces flame and detonation, with separation of charcoal and formation of hydrochloric acid. If any bubbles pass through without producing inflammation, and mix with the vapour of wood-spirit above the liquid, a still more violent explosion is produced. (Kane.)—Wood-spirit shaken into a bottle filled with dry chlorine gas gives out scarcely any heat, and acts but slowly even in sunshine. Also when wood-spirit is distilled in the shade and in a stream of chlorine gas, decomposition takes place so slowly that the distillation in chlorine must be frequently repeated before the formation of hydrochloric acid ceases. In this reaction, there are produced, in addition to hydrochloric acid, two chlorinated liquids of very different volatility; the less volatile of the two forms a crystalline compound with ammonia. (Dum. Pel.)

When dry chlorine gas is passed through a flask containing wood-spirit, and carefully protected from light (in order to avoid explosion as much as possible), then through a glass condensing-tube with a receiver attached to it,—the wood-spirit being gently heated as soon as the most violent action is over, in order to drive out the hydrochloric acid which forms in large quantity,—two liquids are ultimately found in the flask, the upper one being mobile and strongly acid, and the lower, viscid, of the specific gravity of oil of vitriol, of high boiling point, but distilling easily with water, and having a sharp, biting taste. It contains 21·85 C, 1·36 H, 66·41 Cl and 10·38 O; hence its formula is probably $C^6H^2Cl^3O^2$. When decomposed with alkalis, it yields an acid which exerts a reducing action, and is therefore, perhaps, formic acid, together with a new chlorine-compound which has a lower boiling point, and resembles chloroform, but has a different odour. (Kane.)

In winter and in the shade, dry chlorine gas passed through anhydrous wood-spirit, does not produce fiery explosion, notwithstanding the great evolution of heat which accompanies the action; but in sunshine, combustion and explosion are produced. If the liquid be afterwards warmed and thoroughly saturated with chlorine, two strata are formed; the upper of these is strong aqueous hydrochloric acid, and the lower, which is oily and amounts to ¼ of the wood-spirit used, is methylic chloral (*vid. inf.*).—If, however, the wood-spirit contains water even in small proportion, the action of the chlorine is much more violent; and if the liquid, after perfect saturation with chlorine, be heated towards the end of the process, it does not separate into two strata; but on the addition of water, a small quantity of an oily liquid separates, which, however, is not methylic chloral, but xylitic chloral (*q. v.*) composed of: 29·19 C, 3·09 H, 57·79 Cl, 9·93 O=$C^{12}H^8Cl^4O^2$. The *methylic chloral* obtained

with anhydrous wood-spirit [which, however, by no means corresponds to the chloral of alcohol], forms, after washing with water and drying with chloride of calcium, a pale yellow oil, much heavier than water, having a pungent odour which excites tears, and a biting taste. This oil contains 24·16 C, 2·71 H, 59·44 Cl, and 13·69 O; hence its formula is $C^{12}H^6Cl^6O^6$. It may be distilled without decomposition, the first portions of liquid which pass over being colourless, and the latter portions somewhat yellowish, but very little altered in composition. It is not decomposed by carbonate of potash; but caustic potash converts it into chloride of potassium, formiate of potash, acetate of potash, and sesquichloride of formyl, $2(C^2H)Cl^3$, according to the following equation:

$$3C^{12}H^3Cl^6O^6 + 9KO + 8HO = 9KCl + 2C^2H^2O^4 + 6C^4H^4O^8 + 2C^4H^2Cl^6.$$

(Weidmann & Schweizer, *J. pr. Chem.* 23, 12.)—Considering the discrepancy between Kane's analysis and that by Weidmann & Schweizer,—the improbability that chlorine should convert a compound containing only 2 At. C into another containing 12 At. C, and that acetic acid containing 4C should be produced from wood-spirit containing 2C—besides the extremely complicated numerical relations in the decomposition of the compound by potash, and the improbable formula of the so-called sesquichloride of formyl,—it is certainly desirable that the decomposition-product of wood-spirit by chlorine should be prepared in a state of purity and further examined.

¶ Bouis finds that when dry chlorine is passed through [pure?] wood-spirit in diffused daylight, the liquid becomes heated, acquires a transient rose-colour, and gives off hydrochloric acid, a combustible gas which burns with a green flame, and afterwards carbonic acid; and if the passage of the chlorine be stopped as soon as an oily liquid collects at the bottom of the vessel, and the liquid then left to itself for a few hours, a large quantity of funnel-shaped crystals are formed in it, having the composition $C^{10}H^{10}Cl^2O^4$. They are insoluble in water, easily soluble in alcohol and ether, permanent in the air, and volatile; they melt at 50°, forming a liquid which begins to boil at 75°, but is then decomposed, with constant rise of boiling point. Bouis designates these crystals by the name of *chloromesitate* of *methylene*; and supposes the compound to be formed from *methylal*, $C^6H^8O^4$, as follows:

$$2C^6H^8O^4 + 8Cl = C^{10}H^{10}Cl^2O^4 + 2CO^2 + 6HCl.$$

The methylal may either have been formed from the wood-spirit by the action of chlorine; thus:

$$3C^2H^4O^2 + 2Cl = C^6H^8O^4 + 2HCl + 2HO;$$

or, considering the great difficulty of purifying wood-spirit, it may have been already present in that liquid.—If the action of the chlorine on the wood-spirit be further continued, the crystals already formed disappear, and the whole liquid becomes oily. The ultimate product is an oily liquid which, when washed and dried, has the composition $C^6H^3Cl^3O^2$. When this oily liquid (whose vapour irritates the eyes strongly and attacks the skin) is exposed, without washing, to the air, it solidifies in white crystals, having a mother-of-pearl lustre, and easily soluble in water, alcohol, and ether. The aqueous solution is not precipitated by nitrate of silver, and yields the compound in large regular crystals, which have but a faint odour. They melt at 35°, and the liquid begins to boil at 75°, but undergoes decomposition attended with rise of boiling

point. The composition of these crystals corresponds to the formula, $C^6H^2Cl^4O^2 + 8HO$. Alkalis act strongly upon them. In vacuo, they give off water and effloresce. Distilled with anhydrous phosphoric acid, they yield a colourless volatile liquid, $C^6H^2Cl^4O^2$, which, when exposed to the air, absorbs water, and is converted into crystals. The compounds, $C^6H^3Cl^3O^2$, and $C^6H^2Cl^4O^2$, may be regarded as acetone, in which part of the hydrogen is replaced by chlorine. (*N. Ann. Chim. Phys.* 21, 111; abstr. *Jahresber. L. & K.* 1847–8, 670.) ¶

By distilling wood-spirit with oxide of manganese and hydrochloric acid a yellowish distillate is obtained, which, after being washed with water, is colourless, not inflammable, has an unpleasant odour and sour taste: *Huile chloromethylique.* (Aimé, *Ann. Chim. Phys.* 64, 219; also *J. pr. Chem.* 12, 188.)

A solution of 16 pts. of good chloride of lime, decanted from the insoluble portion and distilled with 1 part of wood-spirit, yields chloroform (Dum. Pel):

$$C^2H^4O^2 + 4Cl = C^2HCl^3 + 2HO + HCl.$$

4. Aqueous wood-spirit mixed with potash and then with iodine or bromine till the liquid begins to show turbidity, and then gently evaporated, yields iodoform or bromoform. (Lefort, *Compt. rend.* 23, 229.)

5. Strong nitric acid acts violently on wood-spirit when heated, evolving vapours of hyponitric acid, formic acid, and sometimes also of nitric ether. (Dum. Pel.)—With the weaker commercial acid, wood-spirit may be distilled without decomposition; it is only towards the end of the distillation that small quantities of the three products above-mentioned are given off. (Dum. Pel.)—A mixture of equal volumes of wood-spirit and concentrated nitric acid, heated in a test-tube placed in the water-bath, exhibits some degree of intumescence, and when half the liquid has distilled off, leaves a yellowish liquid free from oxalic acid. (Gm.)—A mixture of wood-spirit, nitric acid and iodine, set aside for some time, deposits yellow crystals; if bromine be substituted for iodine, a heavy oil is produced. (Aimé, *Ann. Chim. Phys.* 64, 219; also *Ann. Pharm.* 23, 260.)

6. When wood-spirit is heated in a retort with nitrate of silver and nitric acid, as in preparing fulminating silver with alcohol, only a feeble action takes place. At first a tolerably large quantity of nitric ether passes over, and on boiling the liquid, a white, pulverulent precipitate of oxalate of silver is deposited, which becomes more considerable the longer the mixture is maintained in a state of ebullition, and wood-spirit and fuming nitric acid added to it. (Dum. Pel.)—When wood-spirit is mixed with acid mercuric nitrate, a precipitate is immediately formed, consisting of a yellowish white, resinous mass, which rapidly increases on boiling the liquid for a short time, and consists of a mixture of 2 At. mercuric formiate with 1 At. mercurous nitrite; but by continued boiling with strong nitric acid, it is converted into white, pulverulent mercuric oxalate. (Dum. Pel.)—The yellowish white, resinous precipitate contains 75·30 mercury, 4·80 C, 0·44 H, 2·7 N, and 16·76 O, and corresponds nearly to the formula $Hg^4C^4H^2NO^{12} = 2C^2HHgO^4 + Hg^2O,NO^5$. (Dum. Pel.) [The formula does not agree sufficiently well with the analysis.]

7. Wood-spirit mixes with oil of vitriol, producing great evolution of heat, sufficient to convert a large portion of the wood-spirit into sulphomethylic acid, which crystallizes by spontaneous evaporation. (Dum. Pel.)

A mixture of 1 pt. wood-spirit and 4 pts. oil of vitriol turns brown and blackens when distilled, not swelling up so much, however, as a similar mixture made with alcohol; and from the beginning to the end of the action, gives off methyl-ether gas, accompanied by carbonic and sulphurous acid, as well as by the alliaceous vapours of sulphate of methyl.—If the mixture contains 8 or 10 parts of oil of vitriol to 1 pt. of wood-spirit, the distillate consists chiefly of sulphate of methyl. (Dum. Pel.)

The higher the temperature of the mixture of wood-spirit and oil of vitriol rises, the smaller is the quantity of methylic ether, and the larger the quantity of sulphate of methyl which passes over; the latter is also found in the residue. (Weidmann & Schweizer.)

A mixture of equal parts of wood-spirit and oil of vitriol yields when heated, first wood-spirit, then sulphurous acid, a light oil (= methol = dumasin), acetic acid, and sometimes also sulphate of methyl. A mixture of 1 pt. wood-spirit and 4 pts. oil of vitriol is very dark brown-coloured and viscid; when distilled, it swells up strongly, and does not give off a light oil, but two strata of liquid, the upper of which is watery, and contains sulphurous acid, acetic acid, sulphomethylic acid and acetate of methyl, together with a very small quantity of wood-spirit,—and the lower, an oily mixture of sulphurous acid, sulphate of methyl and acetate of methyl.—With 10 parts of oil of vitriol the same products are obtained, excepting that the proportion of sulphate of methyl is much larger, and that of acetate of methyl much smaller.—In all these distillations a carbonaceous matter remains in the retort. (Weidmann & Schweizer, *Pogg.* 43, 593.)

On heating a mixture of 1 pt. wood-spirit and 8 or 10 pts. oil of vitriol, till it begins to solidify by carbonization, and no longer gives off any combustible gas—washing the residue repeatedly with water—boiling it with dilute ammonia, and then with water, till the water no longer takes up sulphuric acid,—there remains a carbonaceous mass which, after drying, contains 67·14 C, 1·73 H, 29·73 O, and 1·40 S. (Erdmann & Schweizer, *J. pr. Chem.* 21, 302.)

Anhydrous sulphuric acid dissolves, with evolution of heat, in anhydrous wood-spirit, forming a red-brown solution. If this solution contains excess of wood-spirit, it begins to boil at 75°, and from that temperature to 135° gives off unaltered wood-spirit, but if more strongly heated, evolves a large quantity of methylic ether; at 160° a certain portion of oil likewise passes over; and at 185° the mixture swells up, giving off sulphurous acid and hydrocarbons.

8. Two parts of wood-spirit mixed in a retort with 2 pts. oxide of manganese, and a cooled mixture of 3 pts. oil of vitriol and 3 water, and heated in the water-bath, till gas begins to escape, but no longer, yield a distillate consisting of formal, wood-spirit, aldehyde, and a small quantity of lignone. If the mixture be then heated above 100°, a large quantity of pure formic acid passes over. If undiluted oil of vitriol be used, the mass swells up and becomes very hot. (Kane.)

9. Fluoride of boron converts wood-spirit into methylic ether.—Anhydrous wood-spirit absorbs gaseous fluoride of boron, forming a liquid which fumes in the air, begins to boil at 80°, giving off first wood-spirit with fluoride of boron, then at 130°, a compound of methyl-ether with fluoride of boron, which condenses at 0° to a liquid which burns with a green flame, and gives off methyl-ether when treated with potash; at 150°, pure methyl-ether gas is given off, and between 175° and 200°, an

acid oil passes over, together with a yellowish white jelly [formed from the silica of the retort] from which water or potash separates a large quantity of gaseous methyl-ether. (Kuhlmann, *Pogg.* 33, 213.)

10. Wood-spirit absorbs but a small quantity of gaseous fluoride of silicium, and if subsequently distilled, gives off, first a portion of the absorbed fluoride of silicium, then wood-spirit mixed with fluoride of silicium, and lastly, at 100°, an oily hydrocarbon. (Kuhlmann.)

11. In phosgene gas, wood-spirit is decomposed with great rise of temperature, yielding hydrochloric acid and formic chlormethyl-ether (Dumas & Péligot):

$$C^2H^4O^2 + 2COCl = HCl + C^4H^3ClO^4.$$

12. Wood-spirit treated with chlorosulphuric acid, $SClO^3$, yields, with great rise of temperature, a mixture containing a large quantity of hydrochloric acid and sulphomethylic acid. (Regnault.)

13. Wood-spirit mixed with *chloride of silicium* becomes very turbid, and yields, when distilled, a black, stinking liquid. (Ebelmen, *N. Ann. Chim. Phys.* 16, 157.)

14. Pentachloride of antimony, sesquichloride of iron, and bichloride of tin, heated with anhydrous wood-spirit, convert it into chloride of methyl, C^2H^3Cl; and if they act only in small quantity, likewise give rise to the evolution of methylic ether, or an ethereal liquid which boils at 60°; at the same time, an oily hydrocarbon passes over, and a resinous or coaly residue is left behind.

Pentachloride of Antimony mixes with anhydrous wood-spirit, producing great heat and intumescence, and becoming coloured, even if cooled by a frigorific mixture. The mixture begins to boil at 75°, giving off, first wood-spirit, then between 100° and 160° hydrochloric acid, together with C^2H^3Cl; afterwards pentachloride of antimony mixes with these two products, and water separates from this distillate a kind of methylic ether which condenses at 0° (different, therefore, from that which is formed by the action of oil of vitriol). At 170°, powder of algaroth is deposited; at 200°, the only products which pass over are hydrochloric acid and a hydrocarbon.

64 pts. (2 At.) of wood-spirit dissolve 160 pts. (1 At.) of *Sesquichloride of Iron*, causing rise of temperature, and forming a thick, glutinous liquid. This liquid begins to boil at 80°, and up to that temperature gives off chloride of methyl, without any wood-spirit. The mass, which becomes continually thicker, gives off, between 100° and 110°, an additional quantity of chloride of methyl, together with a little hydrochloric acid; then, between 120° and 130°, a small quantity of colourless distillate, from which water separates a light ethereal fluid burning with a white flame; and potash liberates gaseous chloride of methyl. At 140° a small quantity of chloride of methyl goes off, together with a large quantity of hydrochloric acid. Between 142° and 150°, no more ethereal products pass over, but merely an acid liquid, from which water separates a trace of oil. The residue in the retort is a steel-grey mixture of charcoal and pure protochloride of iron.—With 128 pts. (4 At.) wood-spirit to 160 pts. (1 At.) sesquichloride of iron, the solution begins to boil at 80°, first giving off wood-spirit, and at 120°, likewise chloride of methyl. Water separates from this distillate a small quantity of a light ether, similar to the above, and potash evolves from it gaseous chloride of methyl. Between 130° and 140°, gaseous chloride of methyl passes off; between 140° and 152°, the same gas mixed with hydrochloric acid;

between 150° and 170°, the latter becomes continually more preponderant; and between 170° and 200°, nothing but hydrochloric acid and water pass over. The residue is similar to the preceding.—With a large excess of sesquichloride of iron, the mixture begins to boil at 50°, giving off C^2H^3Cl and hydrochloric acid; above 169°, only the latter passes over; the light ether above mentioned is not produced at all. (Kuhlmann.)

A mixture of 64 pts. (2 At.) wood-spirit and more than 130 pts. (1 At.) *Bichloride of Tin* begins to boil at 110°; gives off C^2H^3Cl together with hydrochloric acid at 120°, and at 130° yields a distillate consisting of C^2H^3Cl and $SnCl^2$, which crystallizes in rhombic tables. Finally, a large quantity of hydrochloric acid passes over together with an oily substance.—A mixture of 64 pts. (2 At.) wood-spirit and 130 pts. (1 At.) bichloride of tin begins to boil at 90°; boils strongly at 100°, giving off gaseous C^2H^3Cl, not condensable at 0°; gives off, between 120° and 130°, a somewhat colourless distillate, without hydrochloric acid, which, up to 135°, increases to 12 measures per cent. of the original mixture, and from which water takes up bichloride of tin, and separates the same light ether—amounting to half the distillate—as with sesquichloride of iron. This ether boils at 60°, and burns with a white flame, greenish at the edges (probably from admixture of C^2H^3Cl). At 140°, the residue becomes thick and gives off hydrochloric acid; between 150° and 160°, gaseous C^2H^3Cl is obtained, together with hydrochloric acid and a distillate from which potash separates methylic ether; and at 175°, a distillate containing C^2H^3Cl together with $SnCl^2$. There remains a brown tumefied mass, from which water extracts $SnCl^2$, leaving behind a pitchy substance.—When 128 pts. (4 At.) of wood-spirit are mixed with 130 pts. (1 At.) of bichloride of tin, the mixture begins to boil at 80°, first giving off half the wood-spirit, and afterwards behaving as in the preceding experiment. (Kuhlmann.)

15. Wood-spirit heated in a retort with pulverized potash-lime (a mixture of lime and hydrate of potash), gives off a large quantity of hydrogen (together with a very small quantity of carbonic oxide or marsh-gas), leaving a large quantity of formiate of potash:

$$C^2H^4O^2 + HO,KO = C^2HKO^4 + 4H.$$

If hydrate of potash be used without lime, pure hydrogen is given off, but the mixture contains a considerable quantity of oxalate of potash as well as formiate, the oxalate being formed from the formiate [probably from the temperature rising higher]. (Dumas and Stas, *Ann. Chim. Phys.* 73, 121; also *Ann. Pharm.* 35, 137; also *J. pr. Chem.* 21, 273.)—The solution of hydrate of potash or soda in wood-spirit turns brown in the air. (Dum. Pel.)—Strong potash-ley quickly decomposes wood-spirit, forming an oily substance=$C^{20}H^{24}O$. (Weidmann and Schweizer.)

16. Sodium thrown into anhydrous wood-spirit produces considerable rise of temperature, liberates hydrogen gas with violent effervescence, and forms a syrup, yellow at first, but afterwards brown. (Gm.)—Potassium liberates hydrogen gas, and forms a compound of methylate of potash with wood-spirit, $KO,C^2H^3O + C^2H^4O^2$ [$=C^2H^3KO^2,C^2H^4O^2$]. (Weidmann and Schweizer, *J. pr. Chem.* 23, 6.)—The compounds which potassium and sodium form with wood-spirit are very easily obtained in rhombic tables, which, by long exposure to the air are converted into alkaline formiates. (Kuhlmann, *Ann. Pharm.* 33, 103.)—The statement formerly made by Löwig (*Pogg.* 41, 404), that wood-spirit treated with potassium

does not give off hydrogen, proceeds, according to Weidmann and Schweizer, from his having made the experiment with lignone instead of wood-spirit.—According to Williamson, the compounds formed by the action of potassium and sodium on wood-spirit are $C^2H^3KO^2$ and $C^2H^3NaO^2$ (*comp.* p. 17).

Combinations. Wood-spirit mixes in all proportions with *Water.*

Per-centage of Anhydrous wood-spirit, sp. gr. 0·8136, at 15°.
According to Ure (*Phil. Mag. J.* 19, 511):

Density.	Per cent.	Density.	Per cent.	Density.	Per cent.	Density.	Per cent.
0·8136	100·00	0·8674	82·00	0·9008	69·44	0·9344	53·70
0·8216	98·11	0·8712	80·64	0·9032	68·50	0·9386	51·54
0·8256	96·11	0·8742	79·36	0·9060	67·57	0·9414	50·00
0·8320	94·34	0·8784	78·13	0·9070	66·66	0·9448	47·62
0·8384	92·22	0·8822	77·00	0·9116	65·00	0·9484	46·00
0·8418	90·90	0·8842	75·76	0·9154	63·30	0·9518	43·48
0·8470	88·30	0·8876	74·63	0·9184	61·73	0·9540	41·66
0·8514	87·72	0·8918	73·53	0·9218	60·24	0·9564	40·00
0·8564	86·20	0·8930	72·46	0·9242	58·82	0·9584	38·46
0·8596	84·75	0·8950	71·43	0·9266	57·73	0·9600	37·11
0·8642	83·33	0·8984	70·42	0·9296	56·18	0·9620	35·71

Wood-spirit dissolves a small quantity of *Phosphorus*, forming a solution which does not alter when kept from the air. (Zeise, *J. pr. Chem.* 26, 84.)

It dissolves the *Hydrates* of *Potash* and *Soda* in large quantities.

Anhydrous wood-spirit mixed with anhydrous *Baryta* becomes strongly heated and dissolves it abundantly. The solution, if evaporated in vacuo after filtration, leaves a crystalline compound containing the two substances in equal numbers of atoms. The crystals when heated, first give off, without apparent alteration, a liquid resembling wood-spirit; then fuse; give off an oil; and leave a black mixture of charcoal and carbonate of baryta. (Dumas & Péligot.) The compound gives off a gas which smells like methylic ether and burns with a pale blue flame,—sometimes also a small quantity of empyreumatic oil. (Kuhlmann.)—When warm wood-spirit is saturated with dry baryta, the solution yields, on cooling, needles which turn brown in the air. (Dum. Pel.)—Wood-spirit nearly saturated with baryta and then diluted with an equal bulk of water, deposits a portion of the baryta in crystalline laminæ. (Payen, *Ann. Chim. Phys.* 65, 244.)

	Crystallized in vacuo.			Dumas & Péligot.
BaO	76·6	70·53		70·5
$C^2H^4O^2$	32·0	29·47		29·5
$BaO,C^2H^4O^2$	108·6	100·00		100·0

Wood-spirit dissolves *Chloride of Calcium* in large quantity, forming with it a crystalline compound. (Dum. Pel.)—The act of solution is accompanied by a rise of temperature which brings the wood-spirit to the boiling point. As the saturated solution [which is syrupy] cools, the compound crystallizes in long, shining, six-sided tables. When heated alone, it does not give off wood-spirit till the temperature rises much above 100°; and a still higher temperature is required to drive off all the wood-spirit, and leave the chloride of calcium pure; but if diluted with water, it is decomposed at 100°. When exposed to the air, it quickly deliquesces, the wood-spirit evaporating. (Kane.)

	Crystallized.				Kane.
CaCl	55·4	.....	46·40	.....	46·7
$2C^2H^4O^2$	64·0	.....	53·60	.....	53·3
$CaCl,2C^2H^4O^2$	119·4	.....	100·00	.....	100·0

2 At. (64 pts.) of wood-spirit mixed with 1 At. (130 pts.) of *Bichloride of Tin* produce great evolution of heat; hence it is necessary to cool the liquid with a frigorific mixture. If only 1 At. wood-spirit be added, part of the stannic chloride remains uncombined. The garnet-coloured mixture solidifies on cooling, in a mass of colourless crystals.—The solution of *Sesquichloride of Iron* in wood-spirit crystallizes with difficulty. (Kuhlmann, *Ann. Pharm.* 33, 107.)

Wood-spirit exhibits towards salts a solvent power similar to that of alcohol. The sulphates it precipitates from their aqueous solution. (Dum. Pel.)

Wood-spirit dissolves Tartaric Acid.—It mixes with Alcohol, Ether, Oils both fixed and volatile, and dissolves many Resins.

Formic Acid. C^2HO^4.

Marggraf. *Chymische Schrifteen*, 1761, 1, 340.
Afzelius Arvidson & Peter Oehrn. *Diss. de acido formicarum*, Ups. 1777; also *Baldinger's N. Magaz. für Aerzte* 2, 102; also *Leonhardi Uebers. v. Macquer's Wörterb.* 1, 180.
Hermbstädt. *Crell, Ann.* 1784, 2, 209.
Lowitz. *Crell, Ann.* 1793, 1, 221.
Richter. *N. Gegenst.* 6, 135.
Fourcroy & Vauquelin. *Ann. du Mus. d'Hist. Nat.* 1, 333; also *A. Gehl.* 2, 42; also *Gilb.* 15, 470.
Süersen. *A. Gehl.* 4, 3.
Gehlen. *Schw.* 4, 1.
Berzelius. *Ann. Chim. Phys.* 4, 109.
Göbel. *Schw.* 32, 345.—*N. Tr.* 5, 2, 3; 6, 1, 176, and 19, 1, 34.—*Schw.* 65, 155, and 67, 74.
Döbereiner. *Schw.* 32, 344, and 63, 366.—*Gilb.* 71, 107; 72, 200.—*Mag. Pharm.* 14, 10.—*Ann. Pharm.* 3, 141; 14, 186, and 53, 145.—*J. pr. Chem.* 1, 76, and 371.
Liebig. *Ann. Pharm.* 17, 69.

Ameisensäure, Formylsäure, Acide formique.

The acid nature of ants has long been known. Samuel Fischer first distilled these insects; Marggraf, Arvidson & Oehrn, Hermbstädt, and Richter, examined the acid more minutely. Fourcroy & Vauquelin pronounced it to be a mixture of acetic and malic acid, a statement which was afterwards completely refuted by Süersen and by Gehlen. Berzelius, Göbel, Döbereiner, Liebig, and Pelouze, examined the most important relations of this acid.

Sources. In ants, especially in *Formica rufa*, but not in the eggs.—¶ According to Fr. Will (*Froriep's Notizen*, 7, 141; *Jahresber. L. & K.* 1847–8, 546), the active deleterious principle in caterpillars, especially

in *Bombyx processionea*, likewise consists of formic acid. It occurs in the free concentrated state in all parts of the caterpillar, but especially in the fæces, in the yellowish green juice which exudes on making an incision into the insect, and, lastly, in the hollow, very brittle hairs. ¶—In commercial oil of turpentine,—whence it may be extracted by agitation with water. (Wiggers, *Ann. Pharm.* 34, 235.) It is doubtless formed by oxidation in the air; it imparts an acid reaction to the oil, and passes over as an aqueous acid when the oil is distilled with water. (Weppen, *Ann. Pharm.* 41, 294.) When oil of turpentine is kept in leaden vessels, crystals of formiate of lead are sometimes produced. (Laurent, *Rev. Scientif.* 10, 126; also *J. pr. Chem.* 27, 316.)—Fr. Müller (*Arch. Pharm.* [2,] 51, 149) states, though not positively, that formic acid is sometimes produced in a similar manner from oil of lemons.—In the needles of *Pinus Abies*, somewhat more abundantly in those which fall off, than in those which are dried while fresh and green. (Aschoff, *N. Br. Arch.* 40, 274.) In pine-needles, which had been used for litter, and had stood for several months made up into a heap and exposed to the air, the acid was formed so abundantly, that on opening the heap, a very sour smell of ants was emitted; hence it is probable that the acid in ants may be derived from the putrefying needles of various kinds of pine, inasmuch as these insects almost always make their nests therein. (Redtenbacher, *Ann. Pharm.* 47, 148.)—In the mineral water of Prinzhofen, near Straubing. (Pettenkofer, *Kastn, Arch.* 7, 104.)—The juice of *Sempervivum tectorum*, when distilled, yields an acid which reduces the noble metals like formic acid, but forms with mercurous nitrate a white precipitate, from which the metal is not reduced till the mixture is heated. (Döbereiner, *Schw.* 63, 368.) ¶ According to Gorup-Besanez (*Ann. Pharm.* 69, 369), the fruit of the soap-tree (*Sapindus saponaria*) distilled with water and sulphuric acid yields a distillate containing formic and butyric acid. Tamarinds similarly treated yield formic and acetic acids, and emit an odour of butyric acid. Gorup-Besanez considers it not improbable that these acids may be formed by oxidation from the tartaric acid originally contained in the fruits.—Formic acid is also found in the juice of the stinging nettle. (Gorup-Besanez, *Ann. Pharm.* 72, 267.) Also in the juice of flesh of man and other mammalia, together with acetic acid and other acids of the series $(CH)^2O^4$. (Scherer, *Ann Pharm.* 70, 340.) ¶

Formation. In the oxidation of wood-spirit by the air in presence of platinum, or by nitric acid. (Dumas & Péligot.)—2. By heating wood-spirit with a mixture of lime and hydrate of potash. (Dumas & Stas.)—3. In the decomposition of chloroform, bromoform, or iodoform, by potash.—4. In the decomposition of hydrocyanic acid by potash, or by the stronger mineral acids. (Pelouze, *Ann. Chim. Phys.* 48, 395; Geiger, *Ann. Pharm.* 1, 44.)—5. In the decomposition of oxalic acid by heat. (Gay-Lussac, *Ann. Chim. Phys.* 46, 218.)—6. By the combustion of alcohol or ether in the lamp without flame. (A. Connell, *Phil. Mag. J.* 11, 512.—7. In the preparation of iodoform from alcohol, iodine, and potassium. (Bouchardat.)—8. By the action of the air on an alcoholic solution of potash. (A. Connell, *N. Ed. Phil. J.* 14, 231; also *Schw.* 68, 15.)—9. By heating alcohol with nitric acid. (Gaultier de Claubry, *J. Pharm.* 25, 764; Dalpiaz, *N. J. Pharm.* 5, 239.)—10. In the decomposition of chloral or bromal by aqueous potash. (Liebig.)—11. By boiling chloracetic acid with excess of potash. (Dumas.)—12. By heating gelatine with aqueous chromic acid. (Schlieper, *Ann. Pharm.* 59, 1.)—13. By

exposing oil of turpentine to the air, or heating it with aqueous chromic acid. (Weppen, *Ann. Pharm.* 41, 294.)—14. By distilling aqueous tartaric acid with peroxide of manganese. (Döbereiner, *Gilb.* 71, 107.)—15. By distilling the following substances with peroxide of manganese and dilute sulphuric acid: Tartaric acid and cane-sugar (Döbereiner, *Gilb.* 71, 107; *Ann. Pharm.* 3, 144); starch (Wöhler, *Pogg.* 15, 307); mucic acid, milk-sugar, starch, woody fibre, *althæa*-root, fibrin (C. G. Gmelin, *Pogg.* 16, 55); alcohol (C. G. Gmelin, Connell, *N. Ed. Phil. J.* 14, 240; Gm. *Pogg.* 28, 508); suberic acid (Brandes, *N. Br. Arch.* 21, 319); grape-sugar, which likewise yields formic acid when treated with sulphuric acid and chromic acid or ferric oxide (Hünefeld, *J. pr. Chem.* 7, 44);—¶ Albumen, fibrin, casein, and gelatin, which likewise yield formic acid with bichromate of potash and sulphuric acid; in both cases the formic acid is accompanied by other acids of the series $(CH^2)O^4$, and a variety of other products. (Guckelberger, *Ann. Pharm.* 64, 39; abstr. *Jahresber. L. & K.* 1847-8, 847-854.) ¶—When some of these compounds—starch, for example—are thus treated, there is given off, together with the formic acid, a strong-smelling volatile oil (furfurol), which, if the distillate be saturated with a fixed alkali, imparts a yellow colour to the liquid, but passes off or is decomposed when the solution is evaporated. In this impure distillate, and in another obtained from starch, oxide of manganese, and hydrochloric acid, Tünnermann (*N. Tr.* 16, 1, 92; *Kastn. Arch.* 20, 198; *Pogg.* 15, 307) thought that he had discovered two peculiar acids, to which he gave the names of *Pyrogenic* and *Amylenic* acids.—When alcohol is treated with sulphuric acid and oxide of manganese, no oil like furfurol passes over, but a large quantity of acetic acid.—16. Sugar, starch, gum, woody fibre, cereal grains, and other organic substances, yield much more formic acid when distilled with oil of vitriol, or a mixture of that substance with an equal bulk of water, than when treated with sulphuric acid and peroxide of manganese; for the latter converts a considerable quantity of the formic acid into carbonic acid and water. Before carbonization, a volatile oil passes over; but as soon as carbonization takes place, the distillate consists of colourless formic acid. Phosphoric acid, bichloride of tin, and other water-forming substances, act like sulphuric acid. (Emmet, *Sill. Amer. J.* 32, 140; also *J. pr. Chem.* 12, 120.)—These statements have been found correct by Erdmann (*J. pr. Chem.* 12, 124), and Stenhouse (*Phil. Mag. J.* 18, 122; also *Ann. Pharm.* 35, 301).—17. When linseed-oil is heated with oil of vitriol, a large quantity of formic acid passes over, together with sulphurous acid. (Sacc, *Ann. Pharm.* 51, 214.)—¶ 18. Sugar, starch, cotton, &c., treated with chloride of lime containing free lime, yield formiate of lime; if no free lime be present, carbonic acid is produced instead of formic acid: on a solution of sugar the action is very violent. Chloride of lime containing free lime forms, with a solution of gelatine, formiate of lime and ammonia. (Bastick, *Pharm. J. Trans.* 7, 467; *N. J. Pharm.* 14, 20; *Jahresber. L. & K.* 1847-8, 381.)—19. By treating crude oil of asafœtida with caustic soda, acetic acid being likewise formed and sulphuretted hydrogen given off. The gummy portion of asafœtida, when subjected to dry distillation, yields formic acid, with a small quantity of acetic acid.—20. Oil of mustard and oil of garlic treated with nitric acid yield formic acid, together with oxalic acid. (Hlasiwetz, *J. pr. Chem.* 51, 355.) ¶

By distilling aloes with very dilute sulphuric acid, Ed. Simon (*N. Br. Arch.* 29, 186) obtained a distillate which reduced silver-salts like formic

acid; but yielded crystals with oxide of lead different from those of formiate of lead.—In the weathering of brown coal containing iron pyrites, a strong odour of formic acid is often evolved. (Anthen. *Repert.* 88, 105.) —When 4 At. of iron-filings are distilled with 1½ At. tartaric acid ($C^8H^6O^{12}$), the water in the receiver acquires an odour of ants, and the property of reducing metallic oxides. (Artus, *J. pr. Chem.* 12, 251.)—According to Göbel (*N. Tr.* 10, 1, 34), formic acid is produced in the dry distillation of argal. [Not satisfactorily proved.]

Preparation. 1. *In the hydrated state.—a. From Ants.*—Red ants previously mashed, or their expressed juices are distilled; the distillate saturated with potash, soda, oxide of lead or oxide of copper; the solution evaporated, whereupon the volatile oil of ants passes off together with the water; and the residue, or the formiate purified by recrystallization, distilled with dilute sulphuric acid. — *α.* Marggraf distils the ants with water, till half the liquid has passed over, and then distils off the stronger acid from the liquid obtained by pressing the residue.—*β.* Arvidson washes the ants in a bag with cold water; exhausts them repeatedly with boiling water; presses the residue, and distils the liquids thus obtained.—*γ.* Hermbstädt distils the juice expressed from living ants without addition of water.—Richter, and likewise Süersen, distil the ants with 2 or 3 times their bulk of water, till the distillate begins to exhibit an empyreumatic odour; the residue in the retort, which still contains formic acid, Süerson saturates with carbonate of potash; he then filters; precipitates impurities by adding a small quantity of formiate of lead; filters; evaporates; and distils with sulphuric acid. —*ε.* Berzelius distils the mashed ants with water, whereupon a portion of the acid passes over; he moreover presses the residue; digests ⅓ of the juice, consisting chiefly of malic and formic acid, with oxide of lead, and the other ⅔ with carbonate of lime; he then precipitates the malic acid in the latter solution by means of the former solution, which contains lead; after which, he filters, evaporates, and distils with sulphuric acid.—*ζ.* Gehlen neutralizes the ant-juice with carbonate of potash, which he adds in slight excess; precipitates animal matters by ferric sulphate added also in slight excess; filters; precipitates the excess of iron-salt with carbonate of potash; evaporates the liquid to the consistence of syrup; and distils with sulphuric acid.—*η.* Göbel saturates the expressed juice with potash, after freeing it from oil; evaporates; and distils the black-brown residue with ½ oil of vitriol and ½ water.

The very dilute acid obtained by either of these methods is saturated with carbonate of potash (Richter, Süersen), soda (Lowitz, Gehlen), or oxide of copper (Gehlen); and the dried residue—or, when oxide of copper is used, the crystals purified by repeated crystallization—distilled with oil of vitriol (Richter, Gehlen), or with a mixture of 1 pt. oil of vitriol and ½ water (Süersen), or with pulverized bisulphate of potash (Lowitz).—If the quantity of water present be too small, a large proportion of the formic acid is decomposed; hence strong oil of vitriol cannot be used for the distillation.—Any sulphurous acid that may be present is removed by continued digestion with minium; also hydrochloric acid (proceeding from the carbonate of potash) by minium, or better by oxide of silver. (Göbel.)

b. From Tartaric acid.—10 parts of tartaric acid are mixed with 14 parts of oxide of manganese, and from 30 to 45 parts of water, and distilled in a capacious retort. (Döbereiner.)

c. From Sugar or Starch with Peroxide of Manganese and Sulphuric acid.—*α.* A solution of 1 pt. sugar in 2 pts. water is heated to 60° with 2½ or 3 pts. of finely pounded manganese in a copper still, which, as the liquid is very apt to froth up, must have at least 15 times the bulk of the mixture; a third part of a mixture of 3 pts. oil of vitriol and 3 pts. water is then gradually added, whereupon carbonic acid gas loaded with vapour of formic acid immediately escapes with violence. The head and condensing tube must now be quickly put on, and when the violent action has subsided, the other two-thirds of the dilute sulphuric acid added, the mixture being stirred all the while; after which the liquid is gradually distilled almost to dryness. The distillate, which is transparent and colourless, and still contains volatile oil (furfurol), is saturated with chalk (the distillate from 100 pts. of sugar saturates from 31 to 38 parts of chalk); and the filtrate evaporated to the crystallizing point;—or if it be desired to obtain the acid, the distillate is saturated with carbonate of soda, evaporated, and 7 parts of the dry residue distilled with a mixture of 70 pts. oil of vitriol and 4 pts. water. (Döbereiner, *Ann. Pharm.* 3, 144.)—This process is a very good one; but the formic acid which it yields is slightly contaminated with acetic acid. To remove this impurity, the distillate should be saturated, while yet warm, not with carbonate of soda, but with carbonate of lead, and the solution evaporated to the crystallizing point; the more soluble acetate of lead remains principally in the mother-liquor; and the formiate of lead thus obtained must be distilled with a mixture of equal parts of oil of vitriol and water.

β. 1 part of starch is mixed with 4 pts. of finely pounded manganese and 4 parts of water in a copper still; 4 parts of oil of vitriol added by small portions, and with constant stirring; the vessel heated by a straw fire till the contents begin to froth up; the head and condensing tube then put on; and the distillation continued till 4½ parts of the liquid have passed over. This liquid has a density of 1·025 at 10°, and saturates 10·6 per cent. of dry carbonate of soda. If the distillation is performed in a retort instead of a still, it is necessary, in order to prevent frothing over, to take only 3·7 parts of manganese, 3 water and 3 oil of vitriol to 1 part of starch; the retort must have 10 times the bulk of the mixture. The product thus obtained amounts to 3·35 parts of a distillate of sp. gr. 1·042, which neutralizes 15 per cent. of dry carbonate of soda. The distillate obtained either from the retort or from the still is clouded by a white substance; and if the distillation has been carried too far, the liquid also contains sulphurous acid. It must therefore be neutralized with carbonate of lime; milk of lime added in excess to convert the solid acid sulphite of lime into the neutral insoluble sulphite; the filtrate evaporated to dryness; and 10 parts of the resulting formiate of lime distilled, either with 8 pts. oil of vitriol and 4 water—whereby 9 pts. of formic acid are obtained, having a density of 1·075,—or with 8 pts. oil of vitriol and 1½ water, by which a highly concentrated acid is obtained. —The strongest acid that can be prepared in this manner is obtained by distilling 18 pts. of finely pounded formiate of lead with 6 pts. oil of vitriol and 1 pt. water in a chloride of calcium bath. The distillate has a density of 1·110 at 10°. (Liebig.)—¶ The method recommended by Cloez (*N. J. Pharm.* 4, 306) is to mix 500 grm. of starch with 2000 grm. of manganese; place the mixture in a still having a capacity of 25 or 30 litres; add 1 litre of water; then a mixture of 2 kilogrammes of oil of vitriol with 2 litres of water, stirring the mixture well; and distil, adding hot water in proportion as the liquid passes over: from 12 to 15

litres of a strongly acid liquid may be thus obtained over, containing about 412 grammes of formic acid ($C^2H^2O^4$). ¶

d. From Sugar, Starch, or Woody Fibre, with Sulphuric Acid.—One measure of oil of vitriol, 1 measure of water, and 1 measure of rye, wheat, oats, or coarsely bruised maize, are heated together in a glass retort till the liquid boils; one measure of water is added as soon as the mass becomes thoroughly black; the liquid distilled till one measure of distillate has passed over; another measure of water added to the residue; and the distillation repeated with a fresh receiver. The first distillate consists of strong formic acid, generally free from sulphurous acid; the second is very dilute and often contains sulphurous acid; this impurity may be removed by agitating the cold liquid for a short time with peroxide of lead.—The organic matter used in this process, being of a granular nature, does not swell up so much; hence the vessels used need not be so large as those required in the preceding processes. (Emmet, *Sill. Amer. J.* 32, 143.)—Carbonization takes place before boiling, so that there is no occasion to wait till the liquid boils. The addition of water causes the hot mass to froth over; hence it is necessary to let the mixture cool before adding fresh water. In all cases, frothing and boiling over are very likely to be produced by a slight rise of temperature; hence the retort should hold at least five times as much as the volume of the mixture. The distillate is free from acetic acid, but contains furfurol, which may be removed by ether. (Erdmann, *J. pr. Chem.* 12, 124.)—Stenhouse (*Phil. Mag. J.* 18, 122) proceeds in the same manner as Emmet, for the preparation of furfurol and formic acid, excepting that he uses wheat-flour, saw-dust, or chaff, instead of grain.

e. From Oxalic Acid.—An intimate mixture of oxalic acid and very fine quartz-sand is distilled in a glass retort, and the distillate freed from oxalic acid by frequent rectification. This process yields very pure formic acid in a highly concentrated state. (Gerhardt, *N. Ann. Chim. Phys.* 7, 130.)

2. *In the anhydrous state.*—Pulverized formiate of lead dried by heat is introduced into a long glass tube, from 4 to 6 lines in width, one end of which is drawn out into a narrow neck, turned downwards and inserted into a small receiver; sulphuretted hydrogen dried by chloride of calcium is passed into the tube at the other end, till the lead-salt is completely decomposed; a gentle heat applied to drive the formic acid into the receiver; and the acid repeatedly boiled to free it from sulphuretted hydrogen. If the tube be too strongly heated, the acid becomes contaminated with decomposition-products containing sulphur. (Liebig.)—Bineau (*Compt. rend.* 19, 769) passes dry carbonic acid gas through the distillate to drive off the sulphuretted hydrogen, and rectifies it, rejecting the first portion, which still smells of sulphuretted hydrogen.

Properties. The anhydrous acid solidifies at −1° in shining laminæ, which melt at +1°. At ordinary temperatures it forms a thin, transparent and colourless liquid, of sp. gr. 1·2353, which boils at 98·5° (bar. 27 in. 10 lines). (Liebig.)—According to Kopp (*Jahresber.* 1847–8, 68), the sp. gr. is 1·2227, at 0°, and the boiling point 105·3 (bar. 760mm.); according to Persoz (*Jahresber.* 1847–8, 91), the acid boils at 100°.—The vapour density between the temperatures of 111° and 118°, varies from 2·125 to 2·14. (Bineau, *Compt. rend.* 19, 769; also *Pogg.* 65, 424; *Compt. rend.* 23, 416; *comp.* p. 55 of this volume.)—The

anhydrous acid fumes slightly in the air, has a pungent sour taste, and is so corrosive, that a single drop placed upon a soft part of the skin produces intolerable pain, causing the part to swell and turn white, afterwards drawing the skin together and producing a painful ulcer. (Liebig.) The dilute acid has a peculiar pungent and sour smell, and a purely acid taste.

According to Berzelius.			Vol.	Density.
2 C	12	26·09	C-vapour 2	0·8320
2 H	2	4·35	H-gas 2	0·1386
4 O	32	69·56	O-gas 2	2·2186
C^2H^2O	46	100·00	Formic acid vapour 2	3·1892
			1	1·5946

The radical-theory regards this anhydrous formic acid, $C^2H^2O^4$, as *Hydrate of Formic acid*, HO,C^2HO^3, and accordingly assumes the existence of a *hypothetically anhydrous Formic acid* $=C^2HO^3=F$ or Fo, which again is regarded as a compound of the hypothetical radical *Formyl*, C^2H, with 3O. ¶ According to the mode of expression adopted by Gerhardt and Williamson, the compound which is here called anhydrous formic acid will be denoted by the formula $\left.\begin{matrix}CHO\\H\end{matrix}\right\}O$ (equiv. p. 28), which represents it as water, in which 1 At. hydrogen is replaced by the radical CHO; and the hypothetically anhydrous acid or formic anhydride by the formula, $\left.\begin{matrix}CHO\\CHO\end{matrix}\right\}O=C^2H^2O^3$, or water in which both atoms of hydrogen are replaced by CHO. As Gerhardt has succeeded in preparing the anhydrides of benzoic and acetic acid, there is but little doubt that this compound will likewise be obtained. ¶

Decompositions. 1. The vapour of the boiling anhydrous acid may be set on fire *in the air*, and burns with a dull blue flame. (Liebig.)—Platinum-black repeatedly moistened in the air with aqueous formic acid, causes slow combustion of the acid, accompanied by evolution of heat and a hissing noise, the products of the combustion being carbonic acid and water. If the platinum-black has been previously charged with oxygen by exposure to the air, it will oxidize small quantities of the acid, even out of contact of air. Spongy platinum, slightly moistened in the air with formic acid containing not more than 3 At. water, becomes almost instantly red-hot, producing water and carbonic acid. (Döbereiner, *Mag. Pharm.* 14, 10; *Pogg.* 36, 308; *Ann. Pharm.* 14, 10; 17, 67, and 53, 145; *J. pr. Chem.* 1, 76.)—*Chlorine* decomposes the acid and its salts completely, converting them after a while into carbonic and hydrochloric acids (Cloez, *N. Ann. Chim. Phys.* 17, 297):

$$C^2H^2O^4 + 2Cl = 2CO^2 + 2HCl.$$

3. *Nitric acid* decomposes formic acid. (Arvidson.)—4. Aqueous *Iodic* or *Periodic acid* acts violently on formic acid at a boiling heat, evolving carbonic acid and iodine. (Benckiser, *Ann. Pharm.* 17, 258.) At a temperature near 100°, aqueous iodic acid completely converts formic acid, in the course of 20 minutes, into water and carbonic acid; but a trace of hydrocyanic acid prevents the decomposition, even at a boiling heat. (Millon, *Compt. rend.* 19, 271.)

5. *Oil of Vitriol*, at a gentle heat, decomposes formic acid and its

salts, converting it into water and carbonic oxide, with strong effervescence, but without blackening (Döbereiner):

$$C^2H^2O^4 = 2HO + 2CO.$$

6. Formic acid reduces the *oxides* of the *noble metals*, yielding water and carbonic acid. It reduces mercuric oxide with strong effervescence when heated. From mercurous or mercuric nitrate it throws down metallic mercury at a boiling heat; boiled with a solution of mercuric chloride, it throws down calomel. (Göbel, Döbereiner.) Mercuric oxide boiled with a concentrated mixture of formic and acetic acid, dissolves with effervescence, as mercurous acetate, which crystallizes on cooling; whereas the same oxide boiled in pure acetic acid forms a solution of mercuric acetate. (Connell, *N. Edin. Phil. J.* 14, 236; also *Schw.* 68, 15.) Mercuric oxide is not decomposed when heated with an aqueous solution of chloride of calcium and formiate of soda; but on heating it with chloride of calcium and free formic acid, decomposition ensues. Between the medium temperature and 80°, calomel is thrown down in shining scales, accompanied by brisk evolution of carbonic acid and production of formiate of potash (the decomposition being quicker as the temperature is higher); but if the liquid be kept constantly boiling, metallic mercury is thrown down. A hot aqueous solution of corrosive sublimate mixed with formiate of potash or soda, and kept for two or three hours at a temperature between 70° and 80°, deposits all the mercury in the form of calomel; but if kept constantly at a boiling heat, it yields the mercury in the metallic state. (Bonsdorff, *Pogg.* 33, 73.) Silver-oxide and those of its salts which are soluble in water, are reduced by formic acid with the aid of heat; the salts are more quickly reduced by formiate of soda. (Göbel, Döbereiner.) Solutions of gold, platinum, and palladium, are not reduced by continued boiling with free formic acid, because the acid gradually volatilizes; but they are completely reduced by formiate of soda, which in some cases throws down spangles, in others, as with platinum, precipitates a *black* possessing great power of inducing combustion. (Göbel.) The aqueous acid converts platinous oxide and platinate of soda into platinum-black, with brisk evolution of carbonic acid. (Döbereiner, *Pogg.* 28, 180; *Schw.* 66, 289.) At a boiling heat, it reduces protochloride of platinum to the metallic state. (Berzelius, *Pogg.* 36, 8.)—7. *Peroxides* with dilute sulphuric acid convert formic acid into carbonic acid and water. (Liebig.)

8. Formiate of potash, moderately heated with excess of *hydrate of potash*, gives off hydrogen, and is converted into oxalate of potash. (Péligot, *Ann. Chim. Phys.* 73, 220; Dumas & Stas, *Ann. Chim. Phys.* 73, 123):

$$2C^2HKO^4 = C^4K^2O^8 + 2H.$$

Combinations. A. With Water.—*Aqueous Formic acid.*—The anhydrous acid mixes with water without rise of temperature, but the mixture is attended with diminution of density. A mixture of 1 At. acid and 1 At. water obtained from 18 pts. lead-salt, 6 oil of vitriol, and 1 water (p. 273), has a density of 1·110 at 10°; does not solidify at—15°; boils at 106°; is as corrosive as the anhydrous acid; and likewise gives off an inflammable vapour. (Liebig.)—The acid of sp. gr. 1·1168 mixes with 1 pt. of water, without rise of temperature, forming a mixture whose density is 1·060; with 3 parts of water it forms a mixture whose density is 1·0296: slight condensation therefore takes place. (Gehlen.)

B. With Salifiable Bases.—The affinity of formic acid for bases is, according to Arvidson, greater than that of acetic acid. The *Formiates* are obtained by dissolving the bases or their carbonates in the aqueous acid, and evaporating. The formiates of the fixed alkalis ignited out of contact of air leave alkaline carbonates slightly blackened by charcoal, a combustible gas, probably carbonic oxide and hydrogen, being also evolved:

$$C^2HKO^4 = KO,CO^2 + CO + H.$$

The formiates of uranium, bismuth, zinc, cadmium, lead, cobalt, nickel, and copper, when heated to redness, leave a regulus of metal, which at a stronger heat assumes the metallic lustre. (Göbel.) In these decompositions, water, carbonic acid, and carbonic oxide are doubtless evolved:

$$C^2HMO^4 = HO + CO + CO^2 + M.$$

Oil of vitriol heated with the formiates decomposes them, forming a sulphate, water, and carbonic oxide gas, which escapes:

$$C^2HKO^4 + 2SO^3 = KO,SO^3 + HO,SO^3 + 2CO.$$

Platinum-black, moistened with the solution of an alkaline formiate, converts it into carbonate. (Döbereiner, *Ann. Pharm.* 14, 14.) The aqueous solutions of formiates, heated with solutions of the noble metals, *e. g.*, mercury and silver (p. 275) in acids, reduce the metals with evolution of carbonic acid. All formiates are soluble in water: their aqueous solutions form dark red mixtures with ferric salts.

Formiate of Ammonia.—Rectangular prisms with four-sided pyramidal summits, and united in tufts. (Göbel.) Has a fresh pungent flavour, and is not poisonous. (Pelouze.) When suddenly heated in a retort, it is resolved into water and hydrocyanic acid (Döbereiner, *Repert.* 15, 425):

$$NH^3,C^2H^2O^4 = C^2NH + 4HO.$$

When gradually heated, it fuses at 120° without giving off water, but evolves a small quantity of ammonia at 140°, and at 180° it is for the most part resolved into hydrocyanic acid and water, a small portion only volatilizing undecomposed. (Pelouze, *Ann. Chim. Phys.* 48, 399; also *Ann. Pharm.* 2, 87.) To make the decomposition complete, the salt must be heated at the closed end of a bent tube, and the vapour passed over a part of the tube kept at a stronger heat. (Liebig.) The aqueous solution exposed to light in a stoppered bottle for half a year, deposits a large quantity of flakes and becomes alkaline. (Horst, *Br. Arch.* 4, 257.) The salt dissolves readily in water.

Formiate of Potash.—a. Neutral.—Crystallizes with difficulty. When heated, it melts to a liquid, which contains no water, but does not solidify till it cools. (Arvidson, Süersen.) Crystallizes in white translucent cubes, which contain no water of crystallization, and when heated, first decrepitate and then turn black. (Winckler, *Repert.* 31, 456.) Its taste is bitter and saline (Arvidson); caustic at first, but afterwards cooling. (Winckler.) According to Richter, it contains 61·09 per cent. of potash. When subjected to dry distillation, it yields carbonate of potash and a scarcely acid distillate. (Marggraf.) At first it gives off undecomposed acid, then, with sudden intumescence, carbonic oxide, which continues to burn till all the acid is destroyed. (Göbel.) Deliquesces in the air. (Marggraf.)

¶ *b. Acid Salt.*—A solution of neutral formiate of potash in hot concentrated formic acid yields, according to Bineau (*N. Ann. Chim. Phys.* 19, 291, and 21, 183; abstr. *Jahresber. L. & K.* 1847–8, 546), crystalline needles as it cools. The mother-liquor evaporated in vacuo over sulphuric acid and caustic potash, yielded a crystalline mass, part of which was left in vacuo, as long as it emitted any odour of formic acid; another portion was dissolved in alcohol and evaporated to dryness in vacuo. These three preparations contained formic acid and potash in the proportion indicated by the formula, $C^2HKO^4 + C^2H^2O^4$; but the first also contained 2·6 per cent. of water, the second 7·6, and the third 11·0 per cent. The salt has a strongly acid taste, and is highly deliquescent. When dissolved in a large quantity of water and the solution evaporated, it is for the most part converted into the neutral salt. When kept for some time in vacuo, it gives off part of its acid. ¶

Formiate of Soda.—a. Neutral.—Rhombic tables with bevelled lateral faces, or flat four-sided prisms (Göbel), having a saline, bitter taste. (Arvidson, Gehlen.) The crystallized salt melts in its water of crystallization; then gives off the water with strong intumescence; and afterwards solidifies in the form of a pearly, anhydrous salt, which, when ignited, leaves 36·6 per cent. of pure [?] soda. (Göbel.) Does not yield any acid distillate when strongly heated. Dissolves in 2 pts. of water. (Arvidson.) Deliquescent. (Göbel.)

	Anhydrous.			Gehlen.		Richter.
NaO	31·2	....	45·75	48·3	....	58·34
C^2HO^3	37·0	....	54·25	51·7	.....	41·66
C^2HNaO^4	68·2	....	100·00	100·0	.....	100·00

	Crystallized.			Göbel.
NaO	31·2	....	36·20	36·6
C^2HO^3	37·0	....	42·92	43·4
2Aq	18·0	....	20·88	20·0
$C^2HNaO^4 + 2Aq$	86·2	....	100·00	100·0

¶ *b. Acid Salt.*—Obtained by dissolving the neutral salt in strong aqueous formic acid, and evaporating in vacuo. Forms ill-defined crystals, containing acid and base in the proportion represented by the formula, $C^2HNaO^4 + C^2H^2O^4$; they also contain 7 per cent. of water. The properties of this salt are similar to those of the corresponding potash-salt. (Bineau.) ¶

Formiate of Baryta.—Transparent prisms, having a strong lustre and belonging to the right prismatic system.—Right rhombic prisms truncated on the two acute lateral edges with two *t*-faces, and bevelled with two *y*-faces, resting on the obtuse lateral edges; $u' : u = 75° 30'$; $y : y = 82°$. (Bernhardi.) Bitter, permanent in the air (Arvidson); effloresce in warm air. (Gehlen.) The salt turns brown when strongly heated, emitting an odour of burnt sugar; dissolves in 4 parts of cold water, but is insoluble in alcohol. (Arvidson.)

	Crystallized.			Richter.		Gehlen.		Göbel.
BaO	76·6	....	67·43	68·56	.....	68·75	.....	67·74
C^2HO^3	37·0	....	32·57	31·44	.....	31·25	.....	32·26
C^2HBaO^4	113·6	....	100·00	100·00	.....	100·00	.....	100·00

Formiate of Strontia.—Transparent, perpendicularly truncated, six-sided prisms, containing 4 At. water. When heated, they first become opaque and then crumble to a white powder. (For Pasteur's observations on the crystalline form of this salt, *vid. N. Ann. Chim. Phys.* 31, 98.)

Formiate of Lime.—Transparent, compressed six-sided prisms, with acuminated terminal faces (Süersen); also truncated octohedrons and dodecahedrons. (Göbel.) They have a saline, bitter taste, and effloresce in the air with loss of all their water. (Göbel.) The salt decrepitates on live coals; does not yield any acid by dry distillation. Soluble in 8 parts of cold water (in 10 pts. of water at 19°, according to Göbel), insoluble in alcohol. (Arvidson.)

Formiate of Magnesia.—According to Richter, this salt forms very small cubes; according to Arvidson, transparent, slender needles united in tufts. Its taste is first sharp and afterwards bitter; it is permanent in the air. (Süersen.) The crystals do not diminish in weight when heated over the water-bath. (Göbel.) When ignited they swell up, turn black, and are ultimately converted into white carbonate of magnesia. (Bergman.)—They are soluble in 13 parts of cold water, but insoluble in alcohol. (Arvidson.)

	Crystallized.			Richter.		Göbel.
MgO	20	....	35·09	37·58	.....	35·56
C^2HO^3	37	....	64·91	62·42	.....	64·44
C^2HMgO^4	57	....	100·00	100·00	.....	100·00

Cerous Formiate.—White crystalline powder, which does not give off its half-atom of water at 250°. When ignited in a close vessel, it does not leave metallic cerium, as stated by Göbel. When ignited in the air, it first turns yellow, and is subsequently converted into ceric oxide. It is very sparingly soluble in water. (Beringer, *Ann. Pharm.* 42, 144.)—Reddish white, crystalline powder, which gives off all its water of crystallization at 120°. At 200° it passes, without fusing, into a kind of dusty ebullition, gives off carbonic acid and gaseous carburetted hydrogen, and is converted, without blackening, into cerous oxide, which, at a higher temperature, changes to yellow ceroso-ceric oxide. (Liebig.)

				Beringer.
2 CeO	108	....	56·55	56·77
2 C^2HO^3	74	....	38·74	38·92
1 Aq	9	....	4·71	4·31
$2C^2HCeO^4$,Aq	191	....	100·00	100·00

Formiate of Alumina.—May also be obtained by precipitating formiate of baryta with sulphate of alumina in equivalent proportions, and evaporating the filtrate. Crystallizes with difficulty. (Liebig.) Gummy; tastes sharp and rough; after evaporation, it is but sparingly soluble in water. (Arvidson, Richter.) Tastes sweet and rough; reddens litmus slightly; becomes moist in the air; forms a clear solution in cold water; dissolves likewise in hot water, but with instant precipitation of all the alumina. (Göbel.) The solution of the pure salt does not become turbid when heated; but if sulphate of potash be present, it forms a precipitate which redissolves as the liquid cools. (Liebig.)

Formiate of Thorina.—A solution of hydrate of thorina in aqueous formic acid yields, by spontaneous evaporation, crystals which form a clear solution in boiling water, but when digested in cold water, form an acid solution and leave a basic salt. Alcohol dissolves them but sparingly. (Berzelius.)

Vanadic Formiate.—The blue solution of hydrated vanadic oxide in aqueous formic acid, deposits, when evaporated in an open vessel, a blue, opaque, saline mass, easily soluble in water. The solution, if it contains free acid, retains its blue colonr on exposure to the air; but if the excess of acid has been previously driven off by evaporation, the solution becomes dark green in the course of 12 hours.—When a thin film of the solution is left to evaporate in the air, there remains a violet residue, which dissolves but imperfectly in water. (Berzelius.)

Vanadic acid is but very slightly soluble in formic acid. (Berzelius.)

Chromic Formiate.—The solution, when evaporated, leaves a green saline mass. (Berzelius, *Lehrb.*)

Uranous Formiate.—Protochloride of uranium yields, with formiate of soda, a green precipitate, which dissolves, with green colour, in excess of the soda-salt, and does not reappear on further addition of chloride of uranium. But on heating the mixture, it becomes turbid, and deposits a greyish green body containing uranous oxide and formic acid. The colourless liquid filtered from this substance contains a large quantity of formic acid and but little uranium. (Rammelsberg, *Pogg.* 59, 34.)

Uranic Formiate.—Uncrystallizable, glutinous mass, which becomes moist on exposure to the air. (Richter.)

Manganous Formiate.—Formed by dissolving the carbonate. Reddish prisms, which are nearly tasteless; redden litmus slightly; crumble to a white powder when heated; dissolve in 15 pts. of cold water, but are insoluble in alcohol. (Arvidson.) Very small, white prisms, having a sweetish, metallic state, and containing 1 At. water. (Göbel.)

Hot formic acid does not dissolve *Antimonic oxide.* (Göbel.)

Formiate of Bismuth.—Crystals which turn black when ignited, and are easily soluble in water. (Arvidson.)

Formiate of Zinc.—Formed by dissolving the metal or its oxide. Transparent and colourless prisms, which are permanent in the air, and, when heated to redness, first swell up, then liquefy, giving off a pungent vapour, and finally leave oxide of zinc. They dissolve sparingly in water (in 24 pts. at 19°, according to Göbel), and are insoluble in alcohol. (Marggraf, Arvidson.)

	Crystallized.			Göbel.
ZnO	40·2	42·23		43·12
C^2HO^3	37·0	38·86		
2 Aq	18·0	18·91		
C^2HZnO^4,2Aq	95·2	100·00		

Formiate of Cadmium.—Formed by dissolving the oxide or carbonate in hot formic acid. Cubes and rhombic dodecahedrons, having a sweet and rough metallic taste. When heated, they slowly give off their water of

crystallization, and then suddenly decompose, leaving 53·75 per cent. of yellowish brown oxide. They dissolve readily in water. (Göbel.)

	Crystallized.		Göbel.
CdO	64	53·77	53·75
C^2HO^3	37	31·10	
2Aq	18	15·13	
C^2HCdO^4,2Aq	119	100·00	

Stannous Formiate. — Sometimes a white insoluble powder, which turns black at first when ignited; sometimes a gelatinous mass, which is difficult to dry, and from which alcohol precipitates a white powder. (Arvidson.)

Stannic Formiate.—Aqueous bichloride of tin mixed with formiate of soda does not become turbid till the mixture is heated; it then becomes white and gelatinous, and after a while the precipitate assumes a crystalline character. (Liebig.) The acid does not dissolve stannic oxide even when heated.

Formiate of Lead.—White prisms, having a strong lustre, and a sweet, astringent taste like that of sugar of lead. (Marggraf, Arvidson.)—The crystals contain no water of crystallization (Berzelius, Lecanu, *J. Pharm.* 8, 552); they contain 5·83 per cent. of water, which they give off at 100°. (Göbel.)—The salt when heated decrepitates forcibly, swells up, turns black, and yields a distillate consisting of a stinking water, which does not exhibit any acid reaction. It dissolves in 36 parts of cold water (Arvidson), and is nearly insoluble in alcohol. In consequence of the small solubility of this salt in water, formic acid added to a cold concentrated solution of subacetate of lead, produces radiating needles of formiate of lead. (Döbereiner.)

	Crystallized.		Berzelius.	Lecanu.	Göbel, at 100°.
PbO	112	75·17	74·88	74·88	75·50
2 C	12	8·05	8·28		7·97
H	1	0·67	0·71		0·75
3 O	24	16·11	16·13		15·78
C^2HPbO^4	149	100·00	100·00		100·00

Ferrous Formiate.—Formed by dissolving the hydrate. The colourless solution covers itself with a metallic film. When heated it becomes turbid, ferrous oxide [?] being separated and formic acid set free, so that we cannot obtain a definite salt. (Göbel.)—The colourless filtrate obtained after precipitating formiate of baryta with ferrous sulphate, leaves, when evaporated in the air, a yellow basic salt of ferric oxide. (Liebig.)

Ferric Formiate. — Small, rough, reddish yellow needles, easily soluble in water, sparingly in alcohol. (Marggraf, Arvidson.) Ferric hydrate, even when recently prepared, dissolves but sparingly in formic acid; the solution, which is brownish yellow, very acid, and has a sweetish, rough taste, leaves, on evaporation, a red-brown, deliquescent, crystalline mass. (Göbel.)—When the dark yellowish red mixture of formiate of soda and a ferric salt is boiled, nearly all the oxide is deposited in the form of a basic salt, so that the liquid contains free formic acid. The *basic salt* thus separated contains 76·125 per cent. of ferric oxide, probably therefore 3 At. ferric oxide to 2 At. formic acid [or

rather 2 : 1]. When subjected to dry distillation, it gives off carbonic acid, and afterwards formic acid with an extremely pungent odour. (Döbereiner, *J. pr. Chem.* 1, 371.)

Formiate of Cobalt.—Rose-coloured, ill-defined crystals, which, when ignited, first turn blue and then black; they are sparingly soluble in water, and quite insoluble in alcohol. (Arvidson.)

Formiate of Nickel.—Green crystals, aggregated in tufts; when ignited, they first turn yellow and then black. (Arvidson.)

Cupric Formiate. — *a. Basic.*— Green, sparingly soluble powder. (Arvidson.)

b. Neutral.—Greenish blue, transparent prisms (having nearly the form of *Fig.* 65). Sp. gr. 1·815. Yield a bluish white powder. (Bernhardi & Gehlen). Prisms belonging to the oblique prismatic system (*Fig.* 96; cleavage parallel to *i*). (J. Müller, *Pogg.* 35, 472.)—The crystals effloresce in warm air, and burn with a green flame in the fire. (Arvidson.) When subjected to dry distillation, they fuse; become dry again and assume a darker blue colour after parting with their water; then give off 2 volumes of carburetted hydrogen gas [probably 1 vol. carbonic oxide and 1 vol. hydrogen] to 1 vol. carbonic acid, and 32·7 per cent. of an acid non-ethereal distillate, leaving a residue of pure copper unmixed with charcoal, and amounting to 28·5 per cent. (Gehlen.) — Dissolves in 7 parts of cold water (Arvidson), in 8·4 parts (Gehlen), forming a blue solution, and in 400 parts of 80 per cent. alcohol. (Gehlen.)

	Crystallized.			Göbel.		Gehlen.
CuO	40	....	35·40	35·83	.....	35·5
C^2HO^3	37	....	32·74	31·66	.....	64·5
4Aq	36	....	31·86	32·50		
C^2HCuO^4,4Aq	113	....	100·00	99·99	.....	100·0

Mercurous Formiate. — When mercuric oxide is dissolved in cold aqueous formic acid, containing 10 per cent. of the anhydrous acid ($C^2H^2O^4$), and a gentle heat then applied, the solution suddenly solidifies, with intumescence and escape of carbonic acid, yielding a micaceous mass; this effect is due to the separation of the mercurous salt formed by the action of the formic acid on the mercuric oxide.—At first, a solution of mercuric formiate is produced; but on the application of heat, 4 At. of this salt are resolved into 2 At. mercurous formiate, 1 At. free formic acid, and 2 At. carbonic acid:

$$4C^2HHgO^4 = 2C^2HHg^2O^4 + C^2H^2O^4 + 2CO^2.$$

As formic acid is set free in this process, the liquid separated from the crystals of the mercurous salt may be again saturated in the cold with mercuric oxide, and then, if gently heated, it will yield another crop of crystals of the mercurous salt. If the mercuric solution be too strongly heated, the crystals turn grey from admixture of mercury, and if a still stronger heat be applied, nothing but metallic mercury is precipitated. —The crystals must be dried between bibulous paper at a temperature between 30° and 40°. They are delicate, microscopic, four and six-sided tables, snow-white, with a pearly lustre and greasy to the touch; their taste is saline at first, but afterwards metallic and astringent. They blacken when exposed to light, especially if moist, and likewise, though

more slowly, in the dark. They are decomposed by pressure, or by a heat of 100°, into mercury, carbonic acid, and formic acid:

$$2C^2HHg^2O^4 = 4Hg + C^2H^2O^4 + 2CO^2.$$

When heated in a spoon, they are suddenly decomposed with a hissing noise and leave metallic mercury. Their aqueous solution, when continuously heated, gives off carbonic acid and deposits all the mercury in the metallic state, the liquid being converted into a solution of pure formic acid (as shown in the preceding equation).—The crystals dissolve in 520 parts of water at 17°, more abundantly, but with incipient decomposition in warm water, and are insoluble in alcohol and ether. (Göbel, *N. Tr.* 6, 1, 190; *Schw.* 65, 155;—*comp.* Liebig, *Pogg.* 3, 207.)

	Crystallized.			Göbel.
Hg^2O	208	....	84·9	83·168
C^2HO^3	37	....	15·1	
$C^2HHg^2O^4$	245	....	100·0	

The black precipitate which ammonia forms with mercurous formiate, contains, according to Harff (*N. Br. Arch.* 5, 262), 3 At. mercurous oxide and 1 At. formiate of ammonia.

Mercuric Formiate.—The solution of mercuric oxide in cold, dilute formic acid yields with potash a precipitate which is yellow at first, and with ammonia a white precipitate; but even if kept cold, it likewise, after a few minutes, deposits crystals of the mercurous salt. (Göbel.)—The finely pulverized oxide dissolves in the cold anhydrous acid, forming a syrupy solution, which if left in vacuo over oil of vitriol dries up to a white, crystallo-granular mass, soluble in water. This mass is likewise converted, by the slightest rise of temperature, into white, acicular mercurous formiate, carbonic acid being at the same time evolved and formic acid set free. (Liebig.)

When a mixture of the aqueous solutions of 2 pts. formiate of potash and 2 pts. cyanide of mercury is left to evaporate, shining crystals are obtained, which give off cyanogen when heated, then blacken and fuse, swell up, and leave a residue of carbonate of potash; when heated with oil of vitriol, they give off carbonic oxide and hydrocyanic acid with effervescence. As these crystals contain 21·65 per cent. of potash and 47·41 of mercury, that is to say, nearly equal numbers of atoms of the two substances, they are perhaps composed of 1 At. formiate of potash and 1 At. cyanide of mercury. (Winckler, *Repert.* 31, 459.)

Formiate of Silver.—Formed by dissolving carbonate of silver in cold aqueous formic acid. Transparent rhombohedral crystals, which burn black in the fire, swelling up and emitting an intolerable smell. They are easily soluble in water, but insoluble in alcohol. (Arvidson.)—On mixing concentrated solutions of neutral nitrate of silver and slightly acid formiate of potash, a large quantity of snow-white crystals is immediately precipitated; these crystals under the microscope present the appearance of rhombic six-sided tables. If the solutions are too concentrated, the mixture solidifies in a curdy mass; if they are too dilute, the whole remains in solution.—The salt blackens very quickly on exposure to light and even in the dark, especially if it be moist; hence the crystals, after drying between paper, appear lead-grey. (Göbel.)—On the application of heat, the salt is rapidly decomposed into metallic silver, carbonic acid,

and formic acid. Aqueous potas decomposes it instantly, with rise of temperature. (Liebig.)—*Heated* formic acid does not dissolve oxide of silver, but reduces it. (Göbel.)

Protosulphide of Methyl. $C^2H^3S = C^2H^3,HS$.

REGNAULT. *Ann. Chim. Phys.* 71, 391 ; also *Ann. Pharm.* 34, 26 ; also *J. pr. Chem.* 19, 2 (1840).—CAHOURS. *Compt. rend.* 22, 366.

Hydrosulphuric Methyl-ether, Hydrosulphate of Methylene; Hydrothion-Holznaphtha, Schwefel-Methyl, Methylsulfür, Schwefel-Formafer; Sulfhydrate de methylène, Ether hydrosulfurique de l'esprit de bois.

An alcoholic solution of monosulphide of potassium is prepared by dividing an alcoholic solution of potash into two equal parts, saturating the one with sulphuretted hydrogen, and then adding the other to it, taking care that the quantity of potash in the mixture is rather too great than too small, because an excess of sulphuretted hydrogen would be injurious. Through this mixture, contained in a tubulated retort, gaseous chloride of methyl is passed nearly to saturation, and the product is then distilled at a gentle heat, the receiver being well cooled, and the stream of gaseous chloride of methyl constantly kept up. From the alcoholic distillate, the sulphide of methyl is separated by water as above (Regnault) :

$$C^2H^3Cl + KS = C^2H^3S + KCl.$$

Very thin liquid, of specific gravity 0·845 at 21°. Boils at 41°. Vapour-density = 2·115. Has an extremely unpleasant odour. (Regnault.)

			Regnault.		Vol.		Density.
2 C	12	38·71	39·39	C-vapour	2		0·8320
3 H	3	9·68	9·85	H-gas	3		0·2079
S	16	51·61		S-vapour	½		1·1093
C^2H^3,HS	31	100·00		Vapour	1		2·1492

The gas is therefore monatomic, like the ethers. (Regnault.)

By chlorine in daylight, the compound is rapidly converted, with rise of temperature and formation of hydrochloric acid, into C^2HCl^2S, which is not permanent, and afterwards, in sunshine, into C^2Cl^3S :

$$C^2H^3S + 6Cl = C^2Cl^3S + 3HCl.$$

Chloride of sulphur and bichloride of carbon are, however, formed at the same time. (Cahours.)—Probably in this manner :

$$C^2HCl^2S + 4Cl = C^2Cl^4 + HCl + SCl.$$

Bisulphide of Methyl. $C^2H^3S^2$.

CAHOURS (1846). *Ann. Chim. Phys.* 18, 257; abstr. *Compt. rend.* 22, 362.

Preparation. 1. By passing gaseous chloride of methyl through an alcoholic solution of bisulphide of potassium :

$$C^2H^3Cl + KS^2 = C^2H^3S^2 + KCl.$$

2. By distilling a mixture of sulphomethylate of lime and bisulphide of potassium:

$$C^2H^3CaO^3,2SO^3 + KS^2 = KO,SO^3 + CaO,SO^3 + C^2H^3S^2.$$

The yellowish distillate is rectified; and the portion which distils over between 110° and 112°, dried by chloride of calcium, and again partially distilled.

Transparent and colourless liquid, having great refracting power, and a density of 1·046 at 18°. Boils between 116° and 118°. Vapour-density at 196°=3·298. Has a very persistent and intolerable odour of onions.

		Regnault.		Vol.	Density.
2 C	12	25·53	28·46	C-vapour..... 2	.... 0·8320
3 H	3	6·39	6·35	H-gas 3	.... 0·2079
2 S	32	68·08	67·90	S-vapour..... ½	.... 2·2186
$C^2H^3S^2$	47	100·00	99·71	1	.... 3·2585

The gas is therefore monatomic, like the ethers.

[The composition of this substance is not in accordance with the nucleus-theory. Should it be considered as a compound of 1 At. C^2H^3S and 1 At. $C^2H^3S^3$?]

This compound may be set on fire by a red-hot body, and burns with a blue flame, emitting a strong odour of sulphurous acid.—Chlorine acts violently upon it, producing at first a substance which crystallizes in amber-coloured rhombic tables, but is converted, by the further action of the chlorine, into a yellow, and ultimately into a red liquid, consisting of a mixture of C^2Cl^3S and SCl.—Bromine likewise forms substitution-products. Moderately strong nitric acid acts strongly on the compound, producing sulphuric acid and a peculiar acid which forms, with potash, long slender needles; with baryta, shining colourless tables; and with lime and oxide of lead, soluble crystallizable salts.*—Oil of vitriol dissolves the compound at ordinary temperatures; but decomposes it when heated.—The compound is not altered by distillation over concentrated potash-solution.

It is but very sparingly soluble in water; but, nevertheless, imparts its odour to that liquid. Mixes in all proportions with alcohol and ether. (Cahours.)

Methylene-Mercaptan. $C^2H^4S^2 = C^2H^2,H^2S^2$.

GREGORY. *Ann. Pharm.* 15, 239 (1835).

Sulfhydrate de sulfure de methyle [*Feleforme*].

Formed by distilling in the water-bath, with efficient condensation, a mixture of 1 pt. of a solution of sulphomethylate of lime, and 1 pt. of a solution of sulphide of hydrogen and calcium (both solutions having a density of 1·25), and agitating the distillate with caustic potash, to free it from hydrosulphuric acid:

$$C^2H^3CaO^3,2SO^3 + KS,HS = C^2H^4S^2 + KO,SO^3 + CaO,SO^3.$$

* Muspratt (*Chem. Soc. Qu. J.* 1, 53) gave to this acid the name of *Bisulphimethylic acid*, representing its salts by the formula $C^2H^3MS^2O^5$; more recently, however (*Chem. Soc. Qu. J.* 3, 22), he has found that it is identical with Hyposulphomethylic acid, the formula of whose salts is $C^2H^3MS^2O^6$ (*comp.* p. 298). [W.]

Liquid; lighter than water; boils at 21°; smells like mercaptan, but much more disagreeable.

Somewhat soluble in water.—Forms a yellow precipitate with acetate of lead.—With mercuric oxide, it forms a white compound (1 At. water being separated) which crystallizes from a hot alcoholic solution in shining laminæ, not fusible at 100°. (Gregory.)

Strong hydrochloric acid placed in contact with zinc and sulphide of carbon (or a mixture of equal parts of alcohol and sulphide of carbon), gives off an extremely fetid gas. (R. Böttger, *J. pr. Chem.* 3, 267.)—[Is this gas C^2H^3,S^4, or a mixture of C^2H^3,S^2 with 2HS ?]

Iodide of Methyl. $C^2H^3I = C^2H^3,HI$.

Dumas & Péligot (1835). *Ann. Chim. Phys.* 58, 29.

Methylic Iodide, Hydriodic Methyl-ether; Iodmethyl, Iod-Formafer; Hydriodate de Methylène, Iodure de Methyle [*Schalaforme*].

One part of phosphorus is added, by small portions, to a solution of 8 pts. iodine, in 12 to 15 pts. wood-spirit, contained in a tubulated retort. As the first portions of phosphorus produce a violent action, the remainder must not be added till the boiling has ceased. The mixture is then agitated, heated immediately, and distilled as long as the ether continues to pass over. The colourless residue contains phosphorus, phosphorous acid, and phosphomethylic acid. From the distillate, which is a mixture of wood-spirit and methylic iodide, the latter is precipitated by water, and afterwards rectified in the water-bath over large quantities of chloride of calcium and oxide of lead.

Colourless liquid of sp. gr. 2·257 at 22°; 2·1992 at 0° (Pierre); boils between 40° and 50°; at 43·8° (bar. 750·2^{mm}) according to Pierre; at 42·2° (bar. 752^{mm}) according to Andrews. (*Chem. Soc. Qu. J.* 1, 27.) Vapour-density = 4·883.

			Dum.	Pél.			
2 C	12	8·51		9·0	C-vapour	2	0·8320
3 H	3	2·13		2·2	H-gas	3	0·2079
I	126	89·36		88·8	I-vapour	1	8·7356
C^2H^3HI	141	100·00		100·0		2	9·7755
						1	4·8877

Burns with difficulty, and only in the flame of a lamp, diffusing a large quantity of violet vapours. (Dumas & Péligot.)

¶ On ammonia and the compound ammonias, iodide of methyl acts by substituting one or more atoms of methyl, C^2H^3 = Me, for H, or by adding one or more atoms of methylene, C^2H^2, to ammonia or ammonium, or their analogues. Thus, when heated in a sealed tube with strong ammonia, it forms, in addition to iodide of ammonium, four different iodides, viz., *iodide of methylium*, $(H^3Me)NI$, *iodide of dimethylium*, $(H^3Me^2)NI$, *iodide of trimethylium*, $(HMe^3)NI$, and iodide *of tetramethylium*, Me^4NI. With triethylamine, Et^3N, it forms iodide of *methylotriethylium*, $(MeEt^3)NI$; with aniline, or phenylamine, $(H^2Ph)N$, it forms *iodide of methylophenylium*, or *hydriodate of methylophenylamine*, $(H^2MePh)NI$ or $(HMePh)N.HI$, &c., &c. (Hofmann, *vid.* pp. 320, 321.)—Iodide of methyl distilled with antimonide of potassium, yields iodide of

potassium and a distillate consisting of *Stibmethyl*, Me^3Sb; and this compound, if mixed with more iodide of methyl, yields *iodide of Stibmethylium*, Me^4SbI. (Landolt, *Ann. Pharm.* 78, 91.)

Iodide of methyl heated with zinc yields methyl-gas, and a white crystalline residue which is decomposed by water, producing brilliant flame, and when distilled in an atmosphere of dry hydrogen, yields a colourless, pellucid distillate, consisting of *Zinc-methyl*, C^2H^3Zn. (Frankland.) ¶

Bromide of Methyl. $C^2H^3Br = C^2H^2,HBr$.

BUNSEN. *Ann. Pharm.* 46, 44.

Methylic Bromide, Hydrobromic Methyl-ether, Methylbromür, Brom-Formafer [*Malaforme*].

a. Gas.—Evolved on gently heating the basic perbromide of cacodyl. (Bunsen.)

Colourless gas, of sp. gr. 3·155 and faint ethereal odour. When cooled below −17°, it condenses into a thin, transparent, and colourless liquid.

				Vol.	Density.
2 C	12	12·63	C-vapour	2	0·8320
3 H	3	3·16	H-gas	3	0·2079
Br	80	84·21	Br-vapour	1	5·5465
C^2H^2,HBr	95	100·00		2	6·5864
				1	3·2932

Mixed with oxygen, it explodes violently on the application of flame, yielding carbonic acid, water, hydrobromic acid and free bromine; 100 volumes of the gas yield 104 vol. carbonic acid. Mixed with air, it burns with a yellowish flame. (Bunsen.)

The gas is scarcely absorbed by water or ether; but very readily by alcohol. (Bunsen.)

¶ *b. Liquid.*—50 parts of bromine are carefully dissolved (by small portions) in 200 parts of pure wood-spirit, at a temperature of 5° or 6°, direct sunshine being carefully excluded. To this solution, at a temperature below 5°, seven parts of phosphorus are gradually added, and the liquid slowly heated in the water-bath. The action begins at 7° or 8°, the temperature then rising high enough to melt the phosphorus. When it is over, the liquid is left to cool; the straw-yellow layer at the top decanted off, and distilled carefully, together with that which has already passed over; the distillate washed with very slightly alkaline water, and afterwards with pure water at 0°; then dried over chloride of calcium, and rectified in the water at a temperature not exceeding 20° or 22°. (Pierre, *N. J. Pharm.* 13, 156; *Jahresber. L. & K.* 1847–8, 672.)

Colourless, neutral, strongly smelling liquid, of sp. gr. 1·664 at 0°. Boils at 13° (bar. 759^{mm}), and retains its transparency and fluidity at −35·5°.—The analysis of this compound agrees with the formula, C^3H^3Br (Pierre); but it is evidently different from Bunsen's. There can be little doubt, however, that it is the true bromide of methyl; for its mode of preparation is similar to that of the iodide, and its properties are exactly such as might be looked for in a compound holding an intermediate place between the chloride and iodide of methyl. ¶

Chloride of Methyl. $C^2H^3Cl = C^2H^3,HCl$.

DUMAS & PÉLIGOT (1835). *Ann. Chim. Phys.* 58, 25; also *Ann. Pharm.* 15, 17.
REGNAULT. *Ann. Chim. Phys.* 71, 377; also *Ann. Pharm.* 33, 328; also *J. pr. Chem.* 19, 210.
BUNSEN. *Ann. Pharm.* 46, 32.

Methylic Chloride, Hydrochloric Methyl-ether; Methyl-chlorür, Sulz-Holznaphtha, Salzsaurer Methylenäther, chlorwasserstoffsaures Methylène, Chlorhydrate de methylène, Chlorure de methyle [*Kalaforme*].

Formation and Preparation. 1. By heating 1 part of wood-spirit with 2 pts. common salt and 3 pts. oil of vitriol, and collecting the evolved gas over water, which retains the impurities, such as sulphurous acid, wood-spirit, and methylic ether. (Dumas & Péligot.)—2. Chloride of methyl is likewise produced by heating common salt with sulpho-methylic acid (Dumas & Péligot):

$$C^2H^4O^2,2SO^3 + 2NaCl = C^2H^3Cl + HCl + 2(NaO,SO^3).$$

3. Also by heating basic perchloride of cacodyl. (Bunsen.)

Colourless gas, which does not liquefy at −18°; sp. gr. 1·731 (1·763 according to Bunsen). Smells like ether (according to Bunsen, it is inodorous); has a sweet taste. Its aqueous solution does not redden litmus, or precipitate a solution of silver. (Dumas & Péligot.)

				Vol.	Density.
2 C	12·0	23·81	C-vapour	2	0·8320
3 H	3·0	5·95	H-gas	3	0·2079
Cl	35·4	70·24	Cl-gas	1	2·4543
C^2H^3,HCl	50·4	100·00		2	3·4942
				1	1·7471

1. The dry gas passed through a red-hot porcelain tube is resolved, with deposition of a little carbon, into a mixture of hydrochloric acid gas and methylene-gas (p. 246), together with undecomposed chloride of methyl. (Dum. Pél.)—2. The gas burns in the air with a white flame, green at the edges. 2 volumes of it, exploded with excess of oxygen, consume somewhat more than 3 volumes of the latter, and form 2 vol. carbonic acid gas, besides water, hydrochloric acid, and a small quantity of chlorine, the excess of oxygen abstracting a certain portion of hydrogen from the hydrochloric acid gas. (Dum. Pel.)—3. Chloride of methyl, mixed with chlorine, takes fire on the approach of flame, and burns with a red light. (Bunsen.)—At ordinary temperatures, chlorine does not act on chloride of methyl in diffused daylight; but in sunshine, it converts the gas, with formation of hydrochloric acid, first into $C^2H^2Cl^2$, then into C^2HCl^3 (chloroform), and lastly into C^2Cl^4. (Regnault, *comp.* Laurent, *Ann. Chim. Phys.* 64, 328.)—4. Chloride of methyl, passed through a heated mixture of lime and hydrate of potash, yields hydrogen gas, chloride of potassium, and formiate of potash, which is subsequently

converted into carbonate (Dumas & Stas, *Ann. Chim. Phys.* 73, 157; also *J. pr. Chem.* 21, 377):

$$C^2H^2Cl + 2KO + HO = C^2HKO^4 + KCl + 4H.$$

5. Potassium burns when heated in the gas, and is converted into chloride of potassium, with separation of charcoal. (Bunsen.)—Aqueous ammonia, potash, or oil of vitriol, exerts no action either on the gas or on its aqueous solution.—¶ By the action of chloride of ethyl on phosphide of calcium, P. Thénard has obtained a number of new products which he regards as compounds of the three phosphides of hydrogen, P^2H, PH^2 and PH^3, with 1, 2 and 3 At. methylene, C^2H^2. One of these, viz., $PH^3,3C^2H^2$, which is a powerful base, may also be regarded as $(C^2H^2)^3P = Me^3P$, analogous to methylamine; another, viz., $PH^3,2C^2H^2$, or Me^2P, is a spontaneously inflammable liquid having a most insupportable odour, and analogous to cacodyl, Me^2As. (*Jahresber. L. & K.* 1847-8, 645.) ¶

1 vol. of water at 16° absorbs 2·8 vol. of this gas. (Dumas & Péligot.) —Alcohol absorbs it very abundantly; ether somewhat less. (Bunsen.)

Bichloride of Methylene. C^2H^2,Cl^2.

REGNAULT (1840). *Ann. Chim. Phys.* 71, 377; also *Ann. Pharm.* 33, 328; also *J. pr. Chem.* 19, 210.

Chlorinated chloride of methyl, chlorhaltender Chlorwasserstoffäther des Holzgeists, Chlor-Formafer, Ether hydrochlorique de methylène monochloruré [*Reforme*].

Chlorine and chloride of methyl are brought together, in sunshine, in a glass globe, having two lateral apertures for the admission of the gases and drawn out below into an open neck, which enters air-tight into one of the mouths of a Woulfe's bottle, whilst the other mouth is connected by a bent tube with a second Woulfe's bottle, and this again by a second bent tube with a flask. The second Woulfe's bottle is surrounded with ice, and the flask is immersed in a freezing mixture, in order to condense the very volatile products which are formed. The compound $C^2H^2Cl^2$ condenses in a state of purity in the flask, whilst in the two Woulfe's bottles the chief product collected is chloroform, C^2HCl^3. In the globe there is also condensed a small quantity of sesquichloride of carbon, probably arising from the presence of alcohol in the wood-spirit.

The compound $C^2H^2Cl^2$ is a colourless liquid, of sp. gr. 1·344 at 18°; boiling point 30·5°; vapour-density 3·012. Its odour resembles that of the oil of olefiant gas.

			Regnault.			Vol.	Density.
2 C	12·0	14·15	13·85	C-vapour	2		0·8320
2 H	2·0	2·36	2·43	H-gas	2		0·1386
2 Cl	70·8	83·49	83·43	Cl-gas	2		4·9086
C^2H^2,Cl^2	84·8	100·00	99·71		2		5·8792
					1		2·9396

By the further action of chlorine in sunshine this compound is converted into C^2HCl^3, and ultimately into C^2Cl^4. Mixed with alcoholic potash, it yields only a slight precipitate of chloride of potassium, and passes over nearly undecomposed when heated. (Regnault.)

Monochlorinated Methyl-Ether. C^2H^2ClO.

REGNAULT (1839). *Ann. Chim. Phys.* 71, 396; also *Ann. Pharm.* 34, 29; also *J. pr. Chem.* 19, 271.

Chlor-Holzäther, Chlor-Formäther, Ether methylique monochloruré [*Nakaforme*].

Methyl-ether gas evolved by heating 1 pt. of wood-spirit with 4 pts. oil of vitriol, is passed, first through water and then through potash-ley, to free it from sulphurous and carbonic acid, then through a long chloride of calcium tube, and finally through a tube drawn out to a fine point, into a glass globe having two lateral tubulures at opposite sides, and terminating below in an open neck. Into the other tubulure is also inserted a tube with a narrow neck, by which chlorine gas, previously washed with water and dried by oil of vitriol, is introduced. The points of the tubes by which the gases enter the globe must be placed as far as possible from each other, so that the gases may not come together till they have been well mixed with air and other gases not concerned in the action; otherwise a violent explosion will ensue, shattering the apparatus to pieces. The descending neck of the globe passes into an adapting tube, below which is placed a bottle with a funnel in its mouth, at some distance, however, so that if the globe should burst, the liquid already collected in the bottle may still be preserved.—The globe is exposed to daylight, but not to direct sunshine.—An hour often elapses before the gases begin to act upon each other; but condensation then takes place suddenly, attended with copious evolution of hydrochloric acid gas.—The gases should flow into the globe with moderate rapidity, and in equivalent proportion. If the globe exhibits a yellow tint from excess of chlorine, the supply of methyl-ether gas must not be accelerated, lest a considerable quantity of the explosive mixture should accumulate in the globe, and produce an explosion; but the chlorine-apparatus must be opened, so as to interrupt the stream of that gas till the yellow colour has been removed by a moderate supply of the methyl-ether gas. But, in spite of every precaution, an excess of the methyl-ether gas, even if it does not cause an explosion, will sometimes produce combustion, attended with a red light and deposition of carbon; in that case, the admission of the gases must be stopped till the apparatus has cooled.—The liquid collected in the bottle consists, after rectification, of pure monochlorinated methyl-ether. (Regnault.)

Transparent, colourless, very mobile liquid, of sp. gr. 1·315 at 20°; boils at 105°, and may be distilled without decomposition. Vapour-density, 3·908. Has a suffocating odour, and excites tears, just like phosgene.—Very slowly decomposed by cold water; the undecomposed portion retains its original composition. By the further action of chlorine in a bright light, it is converted into C^2HCl^2O, and ultimately into C^2Cl^2O. (Regnault.)

		Regnault.		Vol.	Density.
2 C	12·0	20·91	20·92	C-vapour 2	0·8320
2 H	2·0	3·48	3·65	H-gas 2	0·1386
Cl	35·4	61·67	61·53	Cl-gas 1	2·4543
O	8·0	13·94	13·90	O-gas ½	0·5546
C^2H^2ClO	57·4	100·00	100·00	1	3·9795

Fluoride of Methyl. $C^2H^3F = C^2H^2,HF$.

DUMAS & PÉLIGOT (1835). *Ann. Chim. Phys.* 61, 193; also *Ann. Pharm.* 15, 59.

Methylic Fluoride, Hydrofluate of Methylene; Fluorwasserstoffsaures Methylen, Methylfluorür, Fluor-Formafer; Fluorhydrate de Methylène [Flalaforme].

Obtained by gently heating fluoride of potassium with sulphomethylate of potash in a glass flask, and receiving the evolved gas over water, which frees it from impurities:

$$C^2H^4O^2,2SO^3 + 2KF = C^2H^3F + HF + 2(KO,SO^3).$$

Colourless gas, having a density of 1·186, and a pleasant ethereal odour.

2 C	12·0	....	35·61	C-vapour	2	....	0·8320
3 H	3·0	....	8·90	H-gas	3	....	0·2079
F	18·7	....	55·49	F-gas	1	....	1·2964
C^2H^3,HF	33·7	....	100·00		2	....	2·3363 1·1681

The gas burns with a flame like that of alcohol, but bluer, giving off fumes of hydrofluoric acid.—2 volumes of this gas exploded with oxygen consume 3 vol. O, and form 2 vol. CO^2. (Dumas & Péligot.)

Copulated Compounds.

Carbomethylic Acid. $C^3H^4O^3,2CO^2$.

DUMAS & PÉLIGOT (1840). *Ann. Chim. Phys.* 74, 6; also *Ann. Pharm.* 35, 283; also *J. pr. Chem.* 13, 369.

Methyl-Kohlensäure, Acide carbomethylique.—Known only in the form of a baryta-salt.

When dry carbonic acid gas is passed through a solution of anhydrous baryta in anhydrous wood-spirit, the baryta salt is separated in the form of a precipitate having a faint pearly lustre; it is afterwards washed with wood-spirit.—The salt is rapidly decomposed by heat, giving off combustible gases, a large quantity of carbonic acid and a small quantity of ethereal liquid, and leaving carbonate of baryta. It dissolves readily in cold water; but the solution gradually becomes turbid, depositing one-half of the carbonic acid in the form of carbonate of baryta, and evolving the rest in the gaseous form with effervescence, so that in a few hours the whole is decomposed, and nothing but wood-spirit remains dissolved in the water. This decomposition is accelerated by heat, and takes place instantly at a boiling temperature. The baryta-salt is insoluble in absolute alcohol or wood-spirit. (Dumas & Péligot.)

				Dumas & Péligot.
BaO,CO^2	98·6	68·67		68·2
3C	18·0	12·53		12·5
3H	3·0	2·09		2·2
3O	24·0	16·71		17·1
$C^3H^3BaO^3,2CO^2$	143·6	100·00		100·0 = $BaO,CO^2 + C^3H^3O,CO^2$

Urethylane. $C^3H^3Ad,2CO^2$.

DUMAS & PÉLIGOT (1835). *Ann. Chim. Phys.* 58, 52.

ECHEVARRIA. *Ann. Pharm.* 79, 110; *Compt. rend.* 32, 597; *N. J. Pharm.* 19, 322; *J. pr. Chem.* 53, 120; *Pharm. Cent.* 1851, 519; *Jahresber.* 1851, 499.

Urethylan, Kohlen-Formamester.

Formation and Preparation. 1. When oxychlorocarbonate of methylene (p. 309) is dissolved in aqueous ammonia, this compound crystallizes out, together with sal-ammoniac, in deliquescent needles. (Dumas & Péligot; *comp.* p. 310.)

2. The same compound is formed when wood-spirit is saturated with vapour of cyanic acid, C^2NHO^2, evolved by heating cyanuric acid, $C^6N^3H^3O^6$. (Liebig & Wöhler, *Ann. Pharm.* 54, 370; Laurent & Gerhardt, *Compt. rend.* 22, 457; Liebig, *Ann. Pharm.* 58, 260.)

3. Aimé (*Ann. Chim. Phys.* 64, 222; also *Ann. Pharm.* 23, 254; also *J. pr. Chem.* 12, 62) passed dry chlorine gas through slightly heated wood-spirit containing cyanide of mercury, and condensed the evolved vapours in a cooled U-tube. He thereby obtained a liquid of sp. gr. 1·25, which boiled at 50°; attacked the eyes; had the odour of chloride of cyanogen and the taste of hydrocyanic acid; burned with a red, green-edged flame; was decomposed in a few days by water, and immediately by ammonia. Aimé regards this product as chlorocyanide of methyl-oxide $= C^2H^3O,2C^2NCl$, but gives no analysis of it. According to Wurtz's experiments (*Compt. rend.* 22, 503) on the action of chloride of cyanogen on alcohol, the products of which are chloride of ethyl and urethane, a body analogous to urethylane, it is conceivable that Aimé's liquid may be a mixture of several products of decomposition, one of which is urethylane.

¶ 4. When gaseous chloride of cyanogen is passed into wood-spirit mixed with water, no action takes place till the liquid becomes saturated with the gas; but when that point is attained, the liquid begins to boil rapidly and becomes turbid, depositing crystals of chloride of ammonium. On separating these crystals by filtration and distilling the filtrate, more chloride of ammonium separates as the liquid becomes more concentrated; and when this is also separated and the filtrate again distilled, changing the receiver when the boiling point reaches 140°, and collecting apart the portion which distils over between that temperature and 180° or 190°, a liquid is obtained, which after a while deposits crystals of urethylane. The formation of this compound is represented by the equation:

$$\underbrace{C^2H^4O^2}_{\text{Wood-spirit.}} + \underbrace{C^2NCl}_{\text{Chloride of Cyanogen.}} + 2HO = \underbrace{C^4H^5NO^4}_{\text{Urethylane.}} + HCl$$

The production of ammonia is due to the decomposition of the chloride of cyanogen by the water present. No evolution of chloride of methyl, or simultaneous formation of carbonate of ethyl, was observed. (Echevarria.)

Properties. Urethylane crystallizes in tables derived from an oblique rhombic prism; is not deliquescent; melts at 52°...55°; solidifies at 52° if dry, but not till cooled to 50° if the least trace of moisture be present; boils at 177°, and volatilizes without decomposition. Vapour-density, 2·62.—100 pts. of water at 11° dissolve 217 pts. of urethylane; 100 alcohol at 15° dissolve 73 pts.; in ether it is less soluble. (Echevarria.)

				Echevarria.		Vol.		Density.
4 C	24	....	32·00	.... 32·05	C-vapour....	4	....	1·6640
5 H	5	....	6·67	.... 6·97	H-gas.....	5	....	0·3465
N	14	....	18·67		N-gas	1	....	0·9706
4 O	32	....	42·66		O-gas	2	....	2·2184
$C^2H^3Ad,2CO^2$....	75	....	100·00			2	....	5·1995
						1	....	2·5997

Decompositions. Urethylane heated with oil of vitriol diluted with an equal weight of water, is resolved into carbonic acid, wood-spirit, and sulphate of ammonia:

$$C^4H^5NO^4 + HO,SO^3 + 2HO = NH^4O,SO^3 + C^2H^4O^2 + 2CO^2.$$

If pure oil of vitriol be used, the liquid blackens, and gives off sulphurous acid mixed with combustible gases.—Potash likewise decomposes urethylane, with formation of wood-spirit, ammonia, and carbonic acid. ¶

Sulphocarbonate of Methyl-oxide. C^2H^3O,CS^2.

Cahours (1845). *Compt. rend.* 23, 821.

When iodine is made to act upon a solution of xanthomethylate of potash in wood-spirit (in the same manner as Zeise proceeded with the xanthethylate of potash), iodide of potassium and sulphur separate out, and a gas is evolved consisting chiefly of carbonic acid. On the addition of water, a heavy oil is deposited from the mixture, and from this oil sulphur separates. The oil is purified by two rectifications:

$$C^2H^3KO^2,C^2S^4 + I = KI + S^2 + CO + C^2H^3O,CS^2.$$

Thin, pale-yellow liquid of sp. gr. 1·143 at 15°. Boils at 172°, passing over without decomposition. Vapour-density = 4·266 (hence it is monatomic). Has a very powerful and persistent odour, somewhat aromatic.

When set on fire, it burns with a bright flame, and yields a large quantity of sulphurous acid.—In contact with chlorine gas, which acts violently on it even in diffused daylight, it is converted into a crystalline body, which, by the further action of chlorine, is transformed into a liquid. —By alcoholic potash it is resolved into methylic mercaptan which remains in solution, and carbonate of potash which is precipitated (Cahours):

$$C^2H^3O,CS^2 + KO + HO = C^2H^4S^2 + KO,CO^2.$$

According to Cahours.					Vol.		Density.
3 C	18	....	29·51	C-vapour	3	....	1·2480
3 H	3	....	4·92	H-gas	3	....	0·2079
2 S	32	....	52·46	S-vapour	1	....	2·2186
O	8	....	13·11	O-gas	½	....	0·5546
C^2H^3O,CS^2	61	....	100·00		1	....	4·2291

Xanthomethylic Acid. $C^3H^4O^2,2CS^2$.

Dumas & Péligot (1840). *Ann. Chim. Phys.* 74, 13; also *Ann. Pharm.* 35, 288; also *J. pr. Chem.* 13, 376.

Methylschwefelkohlensäure, Acide sulfocarbomethylique.

Known only in the form of potash and lime-salts.

Potash-salt.—Crystallizes from a mixture of potash dissolved in wood-spirit and sulphide of carbon, in needles having a silky lustre.

				Dumas & Péligot.
KO	47·2	32·29	31·42	
4 C	24·0	16·42	16·54	
3 H	3·0	2·05	2·37	
4 S	64·0	43·77		
O	8·0	5·47		
$C^3H^3KO^2,2CS^2$	146·2	100·00	= $KO,CS^2 + C^2H^2O,CS^2$.	

Lead-salt.			Dumas & Péligot.
PbO	112	53·08	53·31
4 C	24	11·38	10·92
3 H	3	1·42	1·50
4 S	64	30·33	
O	8	3·79	
$C^3H^3PbO^2,2CS^2$	211	100·00	

Sulphocarbonate of Methyl. C^3H^3S,CS^2.

Cahours (1846). *Compt. rend.* 23, 822.

Schwefelkohlenstoff-Schwefel-Formafer, Sulfocarbonate de sulfure de methyle.

Obtained by distilling together the concentrated solutions of sulphomethylate of lime and sulphocarbonate of calcium; washing with water the yellow oil which collects below the watery distillate; distilling the oil; receiving in a separate vessel the liquid which passes over at 200° and constitutes the greater portion; and purifying it by repeated rectification:

$$C^2H^3CaO^2,2SO^3 + KS,CS^2 = KO,SO^3 + CaO,SO^3 + C^3H^3S,CS^2.$$

Yellow oil, of specific gravity 1·159 at 18°. Boiling point between 200° and 205°. Vapour-density 4·652 (hence it is monatomic). Has a strong and penetrating odour.

Decomposed rapidly by chlorine and bromine, being converted by the latter into a red crystalline substance resembling bichromate of potash and composed of C^2H^2BrS,CS^2.

It is scarcely soluble in water, but mixes in all proportions with alcohol and ether. (Cahours.)

According to Cahours.					Vol.		Density.
3 C	18	....	26·09	C-vapour	3	....	1·2480
3 H	3	....	4·35	H-gas	3	....	0·2079
3 S	48	....	69·56	S-vapour	1½	....	3·3279
C^2H^2S,CS^2	69	....	100·00		1	....	4·6838

Terbasic Borate of Methyl. $3C^2H^3O,BO^3$.

Ebelmen & Bouquet (1846). *N. Ann. Chim. Phys.* 17, 59; also *J. pr. Chem.* 38, 217; abstr. *Compt. rend.* 22, 368.

Drittelborsaures Methyloxyd; Bor-Formester A; Protoborate methylique.

Dry chlorine gas is passed through a red-hot mixture of boracic acid and charcoal, and the resulting mixture of chloride of boron and carbonic oxide is passed into anhydrous wood-spirit, which must be kept cool, because the absorption of the chloride of boron produces heat. As soon as a large quantity of hydrochloric acid gas begins to escape from the liquid together with the carbonic acid, the colourless borate of methyl collects at the top of the brown mixture of wood-spirit and hydrochloric acid. It is decanted and distilled, the portion which passes over when the boiling point becomes stationary being collected apart, and the latter portion twice rectified to free it from hydrochloric acid.—If the wood-spirit is not perfectly anhydrous, the borate of methyl does not separate from the rest of the liquid, but a brown mixture is produced, containing a considerable quantity of chloride of boron. This mixture is distilled, and the distillate collected in a receiver surrounded with ice, where it separates into two layers, the upper of which is purified by repeated rectification, only that portion of the liquid being collected which passes over below 80°.

Transparent, colourless, very mobile liquid, of specific gravity 0·9551 at 0°; boiling point 72°; vapour-density 3·66. Has a penetrating odour somewhat like that of wood-spirit.

Burns without residue, producing a green flame and white fumes of boracic acid.—In contact with water, it is soon resolved into wood-spirit and boracic acid.

6 C	36·0	....	34·68	C-vapour	6	....	2·4960
9 H	9·0	....	8·67	H-gas	9	....	0·6237
3 O	24·0	....	23·12	B-vapour	1	....	0·7487
BO^3	34·8	....	33·53	O-gas	3	....	3·3279
$3C^2H^3O,BO^3$	103·8	....	100·00		2	....	7·1963
					1	....	3·5981

Biborate of Methyl. $C^2H^3O,2BO^3$.

EBELMEN (1846). *N. Ann. Chim. Phys.* 16, 137; also *Ann. Pharm.* 57, 327; also *J. pr. Chem.* 37, 354.

Zweifachboraxsaures Methyloxyd, Bor-Formester B; Perborate methylique.

Equal parts of finely pulverized vitreous boracic acid and anhydrous wood-spirit are mixed in a retort (the mixture is attended with considerable rise of temperature), and heated to 100°....110°. Only a small quantity of liquid passes over, and this must be poured back several times and again distilled till the temperature rises to 110°. The residue is then left to cool in the retort, broken up and digested for 24 hours with anhydrous ether, the liquid decanted, and the ether distilled from it at a heat which ultimately rises to 200°. Biborate of methyl then remains behind.

Transparent, vitreous mass, which at a moderate heat becomes soft and may be drawn out into threads; it greatly resembles the corresponding compound of the ethyl series.

Burns with a beautiful green flame.—Water decomposes it instantly, with great rise of temperature, producing wood-spirit and boracic acid.

				Ebelmen.
2 C	12·0		12·96	
3 H	3·0		3·24	
O	8·0		8·64	
$2BO^3$	69·6		75·16	·70
$C^2H^3O,2BO^3$	92·6		100·00	

Sulphosomethylic Acid. $C^2H^4O^3,2SO^3$.

Hyposulphomethylic acid, Methylunterschwefelsäure (Kolbe); *Acide sulfoformique* (Laurent); *Acide-metholique sulfuré* (Gerhardt).

Discovered and investigated, together with the three allied chlorinated acids, by H. Kolbe in 1845. (*Ann. Pharm.* 54, 174; *comp.* II. 340, 341.)

The preparation of this acid is so intimately connected with that of three others, viz., of the acid $C^2HCl^3O^3,2SO^3$,—the acid $C^2H^2Cl^2O^3$, $2SO^3$,—and the acid $C^2H^3ClO^3,2SO^3$, that it will be most convenient to give a connected description, as Kolbe does, of the preparation of these four acids.

Preparation of Terchloro-sulphosomethylic acid.—$C^2Cl^3HO^3,2SO^3$.—The crystalline compound $CSCl^2O^2$ (or doubled, $C^2S^2Cl^4O^4$), discovered by Berzelius & Marcet (II., 337), is digested at a gentle heat with dilute potash, in such proportion as to neutralize the alkali completely (an excess of the crystalline compound may be removed by boiling). The product is the potash-salt of this acid, which crystallizes on evaporating and cooling the solution, whilst the chloride of potassium produced at the same time, together with any sulphate of potash accidentally formed, remains in the mother-liquor:

$$C^2Cl^4S^2O^4 + 2KO = C^2Cl^3KO^2,S^2O^4 + KCl.$$

The baryta-salt, $C^2Cl^2BaO^2,S^2O^4$, may be obtained in a similar manner, by using baryta-water instead of potash; separating the liquid by filtration from the sulphate of baryta; evaporating to dryness; exhausting the residue with boiling absolute alcohol; filtering to separate chloride of barium; evaporating the filtrate to the crystallizing point, and then leaving it to cool. By dissolving this salt in water,—decomposing it by a slight excess of sulphuric acid,—digesting the filtrate with carbonate of lead to remove this acid completely,—filtering again,—removing the lead by means of sulphuretted hydrogen,—and evaporating,—the crystallized acid is obtained in the separate state (Kolbe):

$$C^2Cl^2BaO^2,2SO^2 + HO,SO^3 = BaO,SO^3 + C^2Cl^2HO^2,2SO^2.$$

Preparation of Bichloro-sulphosomethylic acid.—$C^2Cl^2H^2O^2,2SO^2$.—1. When zinc is dissolved in the aqueous acid, $C^2Cl^2HO^2,2SO^2$, chloride of zinc is formed, together with the zinc-salt of this second acid:

$$C^2Cl^2HO^2,2SO^2 + 2Zn = C^2Cl^2HZnO^2,2SO^2 + ZnCl.$$

From this solution, the zinc is precipitated by carbonate of potash; the filtrate evaporated to dryness; and the residue boiled with 96 per cent. alcohol: the solution, as it cools, deposits crystals of the potash-salt.—2. More easily: By boiling Kolbe's sulphite of protochloride of carbon (II., 339), $C^2Cl^2S^2O^4$ (or, according to Gerhardt, $C^2HCl^2S^2O^4$), with potash; neutralizing the excess by carbonic acid; evaporating to dryness; and separating the potash-salt from the chloride of potassium by boiling spirit, as in 1. For the equations given for this reaction by Kolbe and by Gerhardt, *vid.* Secondary nucleus C^2ClH.

To purify the potash-salt obtained by 1 or 2 from admixed chloride of potassium, it must be recrystallized from the aqueous solution till it no longer produces any turbidity in a silver-solution.

To obtain the acid from the potash-salt, the alcoholic solution of the salt is mixed with sulphuric acid; the liquid filtered from the sulphate of potash; evaporated as far as possible without decomposition; and, if chloride of potassium be present, till all the hydrochloric acid is driven off. The sulphuric acid is then precipitated from the filtrate by baryta-water added exactly in the right proportion; the filtrate evaporated as far as possible; and the residue exhausted by boiling ether, which leaves undissolved any salt that may still be present, and on evaporation leaves the acid in the form of a coloured liquid. To decolorize this acid, oxide of lead is dissolved in it, the lead precipitated by sulphuretted hydrogen, and the liquid filtered. The colouring matter remains with the sulphide of lead, and the filtrate evaporated in vacuo, leaves the crystallized acid.

Preparation of Chloro-sulphosomethylic acid.—$C^2ClH^2O^2,2SO^2$. The aqueous solution of the potash-salt of the preceding acid is mixed with sulphuric acid, and digested with zinc till saturated therewith. The solution is then left to cool; decanted from the crystallized zincate of potash; the rest of the zinc thrown down from it by boiling with carbonate of potash; the filtrate evaporated; and the residue pounded and boiled with 80 per cent. alcohol. On evaporation, the salt $C^2ClH^2KO^2,2SO^2$ is obtained, mixed however with a considerable quantity of unaltered $C^2Cl^2HKO^2,2SO^2$. It must therefore be again treated, as above, with

sulphuric acid and zinc; and on subsequent treatment with alcohol, but little of the latter salt will remain. To convert this portion likewise, the aqueous solution of the residue, acidulated with a small quantity of sulphuric acid, is exposed to the action of two elements of Bunsen's zinc-carbon battery (I., 423),—the current being conducted into the solution by two amalgamated zinc-plates,—till the evolution of hydrogen at the negative pole ceases and zinc is deposited upon it. The zinc is then precipitated from the solution by carbonate of potash; the filtrate acidulated with sulphuric acid; again exposed to the electric current; the solution again precipitated with carbonate of potash; and these operations repeated three or four times, till the whole of the salt is converted into $C^2ClH^2KO^2,2SO^2$, that is to say, till the salt, when ignited, no longer gives off hydrochloric acid, inasmuch as this acid is evolved from $C^2Cl^2HKO^2,2SO^2$, but not from $C^2ClH^2KO^2,2SO^2$. To ascertain whether the conversion is complete, a sample of the solution is evaporated to dryness, and exhausted by boiling with absolute alcohol; the crystals which separate from the alcoholic solution, on cooling, are dried and heated in a test tube; and the condensed drops mixed with solution of silver. There is no method of *separating* the two salts. The liquid subjected to the action of the current must always contain free sulphuric acid; otherwise the salt $C^2ClH^2KO^2,2SO^2$ will be further converted into $C^2H^2KO^2,2SO^2$.— As soon as the salt $C^2Cl^2HKO^2,2SO^2$ has completely disappeared, the liquid is treated with carbonate of potash to precipitate the zinc; the filtrate evaporated to dryness; the residual mass boiled with 80 per cent. alcohol, which leaves behind the sulphate of potash and the greater part of the chloride of potassium; the potash precipitated from the alcoholic filtrate by sulphuric acid in slight excess; the filtrate evaporated till the boiling point rises to 130°, and all the hydrochloric acid is expelled; the viscid residue diluted with water; the solution saturated with carbonate of lead and filtered from the insoluble sulphate of lead; and the filtrate freed from lead by sulphuretted hydrogen, again filtered, and concentrated by evaporation. The residue is the concentrated aqueous acid, $C^2ClH^2O^2,2SO^2$.

Preparation of Sulphosomethylic Acid, $C^2H^4O^2,2SO^2$.—1. A perfectly neutral solution of the potash-salt of the first acid ($C^2Cl^2KO^2,2SO_2$) is treated as above in the circuit of Bunsen's battery. The transformation takes place quietly with great rise of temperature, no hydrogen being evolved at the negative pole, till the whole of the salt is converted into $C^2H^2KO^2,2SO^2$:

$$C^2Cl^2KO^2,2SO^2 + 3HO + 6Zn = C^2H^2KO^2,2SO^2 + 3ZnCl + 3ZnO.$$

After an hour's action of the battery, the liquid becomes so much charged with chloride of zinc, that zinc is deposited at the negative pole. The zinc is then precipitated by carbonate of potash at a boiling heat; the filtrate evaporated to its former bulk, and the current again made to act upon it till the quantity of carbonate of zinc (resulting from precipitation of the chloride of zinc as it forms by the excess of carbonate of potash) increases to such an amount, that zinc is reduced at the negative pole. The solution is then again precipitated by carbonate of potash, and the process repeated, &c. No hydrogen is evolved at the negative pole till 64 parts of zinc (to 100 parts of $C^2Cl^2KO^2,2SO^2$) have been dissolved at the positive pole. The liquid contains, in addition to $C^2H^2KO^2,2SO^2$, likewise $C^2ClH^2KO^2,2SO^2$, and a very large quantity of chloride of potas-

sium. It must, therefore, be evaporated to dryness; the residue boiled with 80 per cent. alcohol; filtered from the chloride of potassium, which for the most part remains undissolved; the alcohol distilled off; and the residue, after being diluted with water and mixed with carbonate of potash, again subjected to the action of the current till the evolution of hydrogen becomes very brisk. This galvanic decomposition (for 70 grammes of $C^2Cl^3KO^2,2SO^2$) occupies altogether about 10 hours.—2. An amalgam of 1 pt. potassium and 100 pts. mercury is immersed in the aqueous solution of $C^2Cl^3KO^2,2SO^2$. Great heat is then evolved, and $C^2H^3KO^2,2SO^2$ is formed, together with potash and chloride of potassium:

$$C^2Cl^3KO^2,2SO^2 + 3HO + 6K = C^2H^3KO^2,2SO^2 + 3KCl + 3KO.$$

No evolution of hydrogen takes place till the transformation is complete. 1 pt. of $C^2Cl^3KO^2,2SO^2$ requires 1 pt. of potassium; if the quantity of potassium be smaller, the salt $C^2H^3KO,2SO^2$ is mixed with $C^2Cl^3HKO^2,2SO^2$ and $C^2ClH^2KO^2,2SO^2$. From the potash-salt yielded by either of these methods, the acid $C^2H^4O^2,2SO^2$ is obtained in the form of a concentrated aqueous solution, in the same manner as the acid $C^2ClH^3O^2,2SO^2$. (Kolbe.)

¶ 2. This acid is likewise formed by the action of nitric acid on sulphocyanide of methyl, C^2H^3,C^2NS^2. To obtain it in a state of purity, the sulphocyanide is distilled with moderately strong nitric acid, the distillate being repeatedly returned into the retort, and, after four or five distillations, evaporated to expel the last traces of nitric acid. The remaining liquid diluted with water, saturated with carbonate of baryta, then filtered and evaporated, yields crystals of sulphosomethylate of baryta, which may be purified by redissolving in water, precipitating by an excess of absolute alcohol, and recrystallizing. From this salt the acid may be obtained in a state of purity, by precipitating the baryta with sulphuric acid, filtering, digesting the filtrate with carbonate of lead, refiltering, and decomposing the lead-salt with sulphuretted hydrogen. (Muspratt.)

3. By distilling bisulphide of methyl with moderately strong nitric acid, and proceeding as above. (Muspratt.)—From his first experiments on this subject (*Chem. Soc. Qu. J.* 1, 45), Muspratt concluded that the acid thus obtained was a peculiar acid, which he called *Bisulphimethylic acid*, containing 1 At. oxygen less than sulphosomethylic (hyposulphomethylic) acid; but from later researches (*Chem. Soc. Qu. J.* 3, 22) he concludes that this opinion was erroneous and that the two acids are really identical. ¶

Concentrated *Sulphosomethylic acid*, $C^2H^4O^2,2SO^2$, forms a thickish inodorous, sour liquid, which does not yield crystals. It is only when the solution contains potash that crystals are deposited, consisting of the potash-salt. (Kolbe.) Bears a high temperature without decomposition. (Muspratt.)

	According to Kolbe.	
2 C	12	12·50
4 H	4	4·17
2 S	32	33·33
6 O	48	50·00
$C^2H^4S^2O^6$	96	100·00

C^2H^3,S^2O^5,HO, *i.e.*, hydrated hyposulphate of methyl (Kolbe); $C^2H^4,2SO^2$, *i.e.*, bisulphate of marsh-gas (Laurent, Gerhardt); $C^2H^4O^2,2SO^2$, *i.e.*, 1 At. wood-spirit + 2 At. sulphurous acid. (Gm.)

At 130° the acid turns brown and begins to decompose.—It is not reconverted into $C^2H^3ClS^2O^4$ or $C^2H^2Cl^2S^2O^6$ by exposure to the sun in spring.

The salts of this acid (Gerhardt's *Metholates sulfurés*) are soluble in water and crystallizable.

Ammonia-salt.—The solution evaporated over oil of vitriol yields long deliquescent prisms.

Potash-salt.—*a. With* 1 *At. Acid.* Crystallizes from a hot saturated solution in 96 per cent. alcohol, in long silky fibres, which cause the whole liquid to solidify into jelly. After pressure between bibulous paper and drying at 100°, the salt is anhydrous. At a red heat it gives off carbonic oxide, a stinking, sulphuretted gas, and water, leaving a mixture of KS^2 and charcoal, whereby it is distinguished from the corresponding potash-salts, in the acid of which H is wholly or partly replaced by Cl.—Becomes somewhat moist on exposure to the air, and dissolves very readily in water. It is insoluble in cold absolute alcohol, and but slightly soluble in the same liquid at a boiling heat.

b. With 2 *At. Acid.* Crystallizes readily from a concentrated solution of sulphosomethylic acid containing potash, in large four-sided prisms, which redden litmus strongly and deliquesce in the air.

With 1 *At. Acid*, at 100°.			Kolbe.		
2 C	12·0		8·94		8·9
3 H	3·0		2·24		2·4
K	39·2		29·21		29·1
2 S	32·0		23·84		
6 O	48·0		35·77		
$C^2H^3KO^2,2SO^2$	134·2		100·00		

With 2 *At. Acid*, at 100°.			Kolbe.		
4 C	24·0		10·42		10·30
7 H	7·0		3·04		3·10
K	39·2		17·03		17·03
4 S	64·0		27·80		
12 O	96·0		4·71		
$C^2H^3KO^2,2SO^2$ + $C^2H^4O^2,2SO^2$	230·2		100·00		

Baryta-salt.—Transparent rhombic tables, very much resembling the baryta-salt of the acid $C^2ClH^3O^2,2SO^2$; permanent in the air. (Kolbe.)—¶ Very soluble in water, but precipitated from that solvent in fine needles by absolute alcohol, and by ordinary spirit of wine. The crystals dried over oil of vitriol, and then heated to 100° for two days, give off 5·25 per cent. (1 At.) of water. At a higher temperature, they are decomposed, giving off sulphurous and sulphuric acid. (Muspratt.)

Dried at 100°.			Muspratt.		
			a.		*b.*
2 C	12·0	7·34	7.23		
3 H	3·0	1·24	1·58		
2 S	32·0	19·56	19·80		
5 O	40·0	25·04	24·65		
BaO	76·6	46·82	46·74	46·72	46·97
$C^2H^3BaO^2,2SO^2$	163·6	100·00	100·00		

The analysis *a* was made with the salt obtained by process 2 (p. 298) from sulphocyanide of methyl; *b*, with salt prepared from the bisulphide (process 3). ¶

Zinc-salt.—Zinc dissolves readily, and with strong evolution of hydrogen gas in the aqueous acid; the solution yields crystals which contain various quantities of water, and redden litmus.

Lead-salts.—*a. Terbasic.*—The solution of the salt *b* boiled with oxide of lead, filtered, and evaporated in vacuo over oil of vitriol, leaves a white, amorphous, saline mass, from the solution of which carbonic acid throws down carbonate of lead.

	Dried at 100°.		Kolbe.
3 PbO	336	79·43	80·2
2 C	12	2·84	2·6
3 H	3	0·71	0·8
2 S	32	7·56	
5 O	40	9·46	
$2PbO,C^2H^2PbO^2,2SO^2$	423	100·00	

b. Monobasic.—The aqueous acid saturated with carbonate of lead, yields, when evaporated over oil of vitriol, large prisms, which are permanent in the air, redden litmus, have the peculiar sweet taste of lead-salts, and contain 1 At. water, which they give off at 100°, becoming opaque at the same time.

	Dried at 100°.		Kolbe.	¶ Muspratt.	
				a.	*β.*
2 C	12	6·03	6·1		
3 H	3	1·51	1·6		
Pb	104	52·26	51·9	51·2	52·7
2 S	32	16·08	16·3		
6 O	48	24·12	24·1		
$C^2H^2PbO^2,2SO^2$	199	100·00	100·0		

	Crystallized.		Muspratt.	
			a.	*β.*
2 C	12	5·78		5·87
4 H	4	1·92		2·01
Pb	104	50·00	49·50	50·45
2 S	32	15·38		
7 O	56	26·92		
$C^2H^2PbO^2,2SO^2$ + Aq.	208	100·00		

Or:			Muspratt.	
			a.	*β.*
$C^2H^2S^2O^5$	87	41·84		
PbO	112	53·84	53·39	54·33
HO	9	4·32	4·27	
$PbO,C^2H^2S^2O^5$ + Aq.	208	100·00		

a. Salt prepared by process 2 (p. 298); *β.* Salt prepared by process 3. In Muspratt's first memoir (*Chem. Soc. Qu. J.* 1, 45), the salt obtained by process 3 is called *Bisulphimethylate of lead*, and represented by the formula, $PbO,C^2H^2S^2O^4$ + Aq. (*comp.* p. 298); but this formula gives: C = 6·00 per cent.; PbO = 56·00, or Pb = 55·58 per cent., numbers which do not agree so well with the analyses as those calculated by the formula in the preceding table.

Copper-salt.—Obtained in very fine crystals by slowly evaporating the aqueous solution. Remarkably soluble. (Muspratt.)

	Anhydrous.				*Crystallized.*			Muspratt.
2 C	12	....	9·45	2 C	12	....	6·98	.... 6·94
3 H	3	....	2·36	8 H	8	....	4·65	.... 4·99
Cu	32	....	25·20	Cu	32	....	18·60	
2 S	32	....	25·20	2 S	32	....	18·60	
6 O	48	....	37·79	HO	88	....	51·17	
$C^2H^3CuO^2,2SO^2$	127	....	100·00	+ 5 Aq.	172	....	100·00	¶

Silver-salt.—Crystallizes very readily in anhydrous, transparent, thin laminæ, which redden litmus, have a sweetish, metallic taste, and are not much altered by exposure to sunshine; their solution is not decomposed when evaporated by heat. (Kolbe.)

	Crystallized.			Kolbe.
2 C	12	....	5·91	..... 5·75
3 H	3	....	1·48	..... 1·55
Ag	108	....	53·20	..... 53·25
2 S	32	....	15·76	.....
6 O	48	....	23·65	.....
$C^2H^3AgO^2,2SO^2$	203	....	100·00	

Chloro-sulphosomethylic Acid. $C^2ClH^3O^2,2SO^2$.

Chlorelayl-Unterschwefelsäure (Kolbe); *Acide sulfoformique chloré* (Laurent); *Acide métholique chlorosulfuré* (Gerhardt).

History, formation, and preparation (pp. 296, 297).

Thickish liquid, syrupy at 16°; strongly acid; yields no crystals; sustains a heat of 140° without decomposition.

	According to Kolbe.		
2 C	12·0	.....	9·20
3 H	3·0	.....	2·30
Cl	35·4	.....	27·15
2 S	32·0	.....	24·54
6 O	48·0	.....	36·81
$C^2ClH^3O^2,2SO^2$	130·4	.....	100·00

C^2H^3,Cl,SO^3+HO (Kolbe); $C^2H^3Cl,2SO^3$. (Laurent, Gerhardt.)

All the salts of this acid are soluble in water, and most of them are crystallizable.

Ammonia-salt.—The aqueous solution, evaporated over oil of vitriol, yields deliquescent prisms.

Potash-salt.—Crystallizes in needles from a hot saturated solution in 96 per cent. alcohol, the liquid thereby becoming semi-solid. The needles pressed between paper and dried at 100°, are anhydrous; at a red heat, they give off water and sulphurous acid with a trace of sulphur, and leave chloride of potassium much blackened by charcoal:

$$C^2ClH^2KO^2,2SO^2 = KCl + 2C + 2HO + 2SO^2.$$

The salt becomes moist in the air, but does not deliquesce. It does not dissolve in absolute alcohol.

	Dried at 100°.			Kolbe.
2 C	12·0	....	7·12	7·0
2 H	2·0	....	1·18	1·2
Cl	35·4	....	21·00	21·2
K	39·2	....	23·25	23·4
2 S	32·0	....	18·98	18·9
6 O	48·0	....	28·47	28·3
$C^2ClH^2KO^2,2SO^2$	168·6	....	100·00	100·0

Soda-salt.—Crystallizes from boiling alcohol of 96 per cent. in needles united in stellate groups, and deliquescent in the air.

Baryta-salt.—Small rhombic tables which redden litmus faintly, and have a cooling, saline taste.

Lead-salt.—*a. Basic.*—The solution of the salt *b*, boiled with lead-oxide, yields an alkaline filtrate which deposits carbonate of lead on exposure to the air.

b. Normal.—The aqueous acid, saturated with carbonate of lead, and evaporated over oil of vitriol, yields delicate silky needles, united in tufts. After being pressed between paper and dried over oil of vitriol, they appear dull and opaque, and retain 3·7 per cent. (1 At.) water, which escapes at 100°.—The salt dissolves very readily in water, forming a solution which reddens litmus and tastes sweet at first, but afterwards astringent.

	Dried at 100°.			Kolbe.
2 C	12·0	....	5·14	4·85
2 H	2·0	....	0·86	0·95
Cl	35·4	....	15·16	
Pb	104·0	....	44·56	44·28
2 S	32·0	....	13·71	
6 O	48·0	....	20·57	
$C^2ClH^2PbO^2,2SO^2$	233·4	....	100·00	

Silver-salt.—The saturated solution of carbonate of silver in the aqueous acid evaporated over oil of vitriol in vacuo and in the dark, leaves a pale yellow viscid liquid, which with difficulty yields small crystals, having a slight acid reaction, a sweetish and disagreeably metallic taste, and very sensitive to light and heat. (Kolbe.)

Bichloro-sulphosomethylic Acid. $C^2Cl^2H^2O^2,2SO^2$.

Chlorformyl-Unterschwefelsäure (Kolbe); *Acid sulfoformique bichloré* (Laurent); *Acid métholique bichlorosulfuré* (Gerhardt).

History, formation, and preparation (p. 296).

Small, colourless prisms, having a very sour taste. They fuse when heated.

	According to Kolbe.		
2 C	12·0	.....	7·28
2 H	2·0	.....	1·21
2Cl	70·8	.....	42·96
2 S	32·0	.....	19·42
6 O	48·0	.....	29·13
$C^2Cl^2H^2O^2,2SO^2$	164·8	.....	100·00

The acid sustains without decomposition a temperature of 140°; at a stronger heat, it emits dense, white, acid fumes, and leaves a residue of charcoal. It is not decomposed by nitric acid, aqua-regia, or chromic acid.—Zinc dissolves in the aqueous acid, liberating hydrogen gas which smells of sulphide of carbon, and forming chloride of zinc, together with the two salts: $C^2Cl^2HZnO^2, 2SO^2$, and $C^2ClH^2ZnO^2, 2SO^2$. The quantity of the latter salt is greater as the evolution of hydrogen is kept up for a longer time by continual addition of sulphuric acid; but complete transformation can only be effected by electric action (p. 297). The mode of formation of the latter salt by zinc is expressed by the following equation:

$$C^2Cl^2H^2O^2,2SO^2 + 2Zn = ZnCl + C^2ClH^2ZnO^2,2SO^2.$$

The acid deliquesces in the air.

It decomposes soluble metallic chlorides, and with bases it forms salts all of which are soluble in water.

Ammonia-salt.—The acid neutralized with ammonia yields, by spontaneous evaporation, transparent and colourless prisms, an inch long and permanent in the air.

Potash-salt.—Preparation (p. 296).—Small, pearly scales which, after drying in vacuo over oil of vitriol, are anhydrous. The salt is neutral, has a slightly saline taste, and is permanent in the air. When heated above 250°, it gives off carbonic oxide, carbonic acid, hydrochloric acid, and sulphurous acid, and leaves a residue of chloride of potassium, mixed with a small quantity of charcoal:

$$C^2Cl^2HKO^2,2SO^2 = KCl + C + CO^2 + HCl + 2SO^2.$$

The carbonic oxide is probably formed by the action of the red-hot charcoal in the residue on the carbonic acid. The salt dissolves in water, and in boiling absolute alcohol, but is insoluble in cold absolute alcohol.

	Dried in vacuo.				Kolbe.
2 C	12·0	....	5·91	.....	5·80
H	1·0	....	0·49	.....	0·55
2 Cl	70·8	....	34·88	.....	35·00
K	39·2	....	19·31	.....	19·76
2 S	32·0	....	15·76	.....	16·00
6 O	48·0	....	23·65	.....	22·89
$C^2HCl^2KO^2,2SO^2$	203·0	....	100·00	.....	100·00

Silver-salt.—The aqueous acid neutralized with carbonate of silver, and evaporated in vacuo over oil of vitriol in perfect darkness, yields small, transparent, tolerably colourless crystals, which, after drying in vacuo or over the water-bath, are free from water. The salt remains undecomposed till heated to 150°, and at higher temperatures is decomposed like the potash-salt. Its aqueous solution is very easily blackened by light or heat. (Kolbe.)

	Crystallized.				Kolbe.
2 C	12·0	....	4·41	.....	4·5
H	1·0	....	0·37	.....	0·5
2 Cl	70·8	....	26·05		
Ag	108·0	....	39·74	.....	39·3
2 S	32·0	....	11·77		
6 O	48·0	....	17·66		
$C^2Cl^2HAgO^2 2SO^2$	271·8	....	100·00		

Methylic Sulphate. C^2H^3O,SO^3.

DUMAS & PÉLIGOT (1835). *Ann. Chim. Phys.* 58, 32; also *Ann. Pharm.* 15, 22.

Sulphate of Methyl, Sulphate of Methyl-oxide, Sulphuric Methyl-ether; Schwefelsaures Methyloxyd, Schwefel-Formester; Sulfate de methylène, Sulfate neutre d'oxyde de methyle.

Preparation. 1. If 1 part of wood-spirit be distilled with 8 or 10 pts. oil of vitriol, keeping the mixture in a state of gentle but constant ebullition, the operation may be carried on to the end without boiling over. The methylic sulphate, which collects in the form of an oil at the bottom of the acid watery distillate, amounts to at least as much as the wood-spirit used. The upper stratum is decanted; the oil agitated with a small quantity of water to remove the sulphuric acid; rectified once over chloride of calcium to dry it; then several times over finely pounded baryta, which retains the sulphurous acid; and finally placed in vacuo over oil of vitriol and hydrate of potash, whereby the wood-spirit and any sulphurous acid that may still be present are removed. (Dumas & Péligot.)—2. When vapour of anhydrous sulphuric acid is passed into a glass globe filled with gaseous methylic ether, the two gases condense together, with great evolution of heat, and form sulphate of methyl, which may be purified from free sulphuric acid by distillation over burnt lime, and from a trace of sulphurous acid by placing it in a vacuum for 24 hours. This is the only known case of the formation of an ether of the third from an ether of the first class. (Regnault, *Ann. Chim. Phys.* 66, 106; also *Ann. Pharm.* 27, 11; also *J. pr. Chem.* 13, 429.)

Colourless oil of specific gravity 1·324 at 22°, boiling at 188° and distilling without decomposition. Vapour-density about 4·565. Has an odour like that of garlic. (Dumas & Péligot.)

			Dumas & Péligot.	Weidmann & Schweizer.		Vol.	Density.
2 C	12	19·05	19·20		C-vapour	2	0·8320
3 H	3	4·76	4·75		H-gas	3	0·2079
O	8	12·70			S-vapour	½	1·1093
SO^3	40	63·49		63·64	O-gas	2	2·2186
C^2H^3O,SO^3	63	100·00				1	4·3678

Methylic sulphate decomposes slowly in cold water, but quickly and with great evolution of heat in boiling water, in wood-spirit, or in sulphomethylic acid (Dumas & Péligot):

$$2(C^2H^3O,SO^3) + 2HO = C^2H^4O^2 + C^2H^4O^2,2SO^3.$$

When this compound is distilled with water, sulphomethylic acid remains in the retort; the milky distillate, however, contains no wood-spirit, but Dumasin (= Methol) rises to the top of it in oily drops. (Weidmann & Schweizer, *Pogg.* 43, 593.) Anhydrous baryta has no action on methylic sulphate, but hydrate of baryta or the aqueous solutions of the fixed alkalis decompose it quickly, and with evolution of heat, into wood-spirit and an alkaline sulphomethylate. (Dumas & Péligot.) When methylic sulphate is distilled with aqueous potash, sulphomethylate of potash remains behind, but the distillate does not contain wood-spirit, but oily

drops of Dumasin rise to the top of it. (Weidmann & Schweizer.)—Löwig (*Pogg.* 42, 409) obtained by this distillation, instead of wood-spirit, an ethereal liquid having a sweet, pleasant taste, and totally different from wood-spirit. When dry ammoniacal gas is passed over methylic sulphate, the latter is converted, with evolution of heat, into a soft crystalline mass, probably a mixture of sulphamethylane and undecomposed methylic sulphate. With aqueous ammonia, methylic sulphate becomes heated so much as to project the mass out of the vessel, and a solution is formed containing sulphamethylane, $C^2HA^3O^2,2SO^3$, and wood-spirit. (Dumas & Péligot.)

$$2\,(C^2H^3O,SO^3) + NH^3 = C^2H^5N,2SO^3 + C^2H^4O^2.$$

Methylic sulphate, heated with the following substances, yields, by a kind of double decomposition, the following ethers of the second and third classes: With fused *chloride of sodium:* chloride of methyl and sulphate of soda:

$$C^2H^3O,SO^3 + NaCl = C^2H^3Cl + NaO,SO^3.$$

With *fluoride of potassium:* fluoride of methyl and sulphate of potash.—With the *sulphides of the alkali-metals:* a liquid resembling mercaptan.—With *cyanide of potassium* or *cyanide of mercury:* a liquid cyanide of methyl.—With *formiate of soda:* formiate of methyl:

$$C^2H^3O,SO^3 + C^2HKO^4 = C^2H^3O,C^2HO^3 + KO,SO^3.$$

With *benzoate of potash:* benzoate of methyl. (Dumas & Péligot.)

Sulphomethylic Acid. $C^2H^4O^2,2SO^3$.

DUMAS & PÉLIGOT. *Ann. Chim. Phys.* 58, 54.
KANE. *Phil. Mag. J.* 7, 397; also *J. pr. Chem.* 7, 96.

Methyl-schwefelsäure, Acide sulphomethylique, Bisulphate de methylène.

When 1 part of wood-spirit is mixed with 2 parts oil of vitriol, the heat evolved is sufficient to induce the formation of this acid; and if the liquid be then left to evaporate spontaneously, the acid often crystallizes. (Dumas & Péligot.)—The mixture of 1 pt. wood-spirit and 2 pts. oil of vitriol is diluted with water; slightly supersaturated with baryta, and filtered from sulphate of baryta; the filtrate concentrated in the water-bath, whereupon a small additional quantity of sulphate of baryta is deposited; and finally, the liquid is placed under a bell-jar, together with quick-lime, and left to evaporate at the temperature of the air till the baryta-salt crystallizes. Into this salt the liquid is converted even to the last drop. By dissolving the baryta-salt in water, precipitating the baryta by adding sulphuric acid in the exact quantity required, and evaporating the filtrate in vacuo to the consistence of a syrup, the acid is obtained in the crystalline form. (Dumas & Péligot.) It may also be prepared by decomposing the lead-salt with sulphuretted hydrogen. It is, however, obtained in the state of greatest purity by leaving a solution of methylic sulphate in boiling water to evaporate spontaneously. (Liebig, *Chim. org.*)

White, strongly acid needles.

The acid decomposes very easily, giving off sulphurous acid in vacuo, even at ordinary temperatures. (Dumas & Péligot.)

It is very soluble in water.

The *Sulphomethylates* are soluble in water. The sulphomethylates of the fixed alkalis, when heated, give off methylic sulphate, C^2H^3O,SO^3, and leave the corresponding alkaline sulphates. (Dumas & Péligot.)

Potash-salt.—Pearly laminæ. (Dumas & Péligot.)—Deliquescent, rhombic tables, which give off their 1 At. water in vacuo over oil of vitriol. The salt when heated gives off water, methylic sulphate, and sulphurous acid, leaving sulphate of potash mixed with charcoal. (Kane.)

	Crystallized.				Kane.
KO	47·2	....	29·65	....	29·51
$2\,SO^3$	80·0	....	50·25	....	50·10
C^2H^3O	23·0	....	14·45	....	14·39
Aq.	9·0	....	5·65	....	6·00
$C^2H^3KO^2,2SO^3 + Aq.$	159·2	....	100·00	....	100·00

$= KO,SO^3 + C^2H^3O,SO^3 + Aq.$

$= \left.\begin{matrix}C^2H^3\\K\end{matrix}\right\}2SO^4 + Aq.$

Baryta-salt.—Colourless, four-sided tables, having a sweet taste. The crystals effloresce in the air at ordinary temperatures; but more quickly in vacuo, giving off 10·2 per cent. (2 At.) of water. When heated, they effloresce with decrepitation, and without fusing; the residue, when more strongly heated, gives off water, sulphurous acid, combustible gases, and methylic sulphate, leaving sulphate of baryta, blackened by a small quantity of charcoal. The salt, when heated in the air, takes fire, and leaves white sulphate of baryta. (Dumas & Péligot.)

	Crystallized.				Dum. Pél.		Kane.
BaO	76·6	....	38·76	....	38·1	....	38·50
$2\,SO^3$	80·0	....	40·49	....	40·8	....	40·21
2 C	12·0	....	6·07	....	6·1		
3 H	3·0	....	1·52	....	1·5	....	11·49
O	8·0	....	4·05	....	3·3		
2 Aq.	18·0	....	9·11	....	10·2	....	9·80
$C^2H^3BaO^2,2SO^3 + Aq.$	197·6	....	100·00	....	100·00	....	100·00

Lime-salt.—Anhydrous octohedrons, very deliquescent. (Kane.)

	Crystallized.				Kane.
CaO	28	.....	21·37	.....	21·41
$2\,SO^3$	80	.....	61·07	.....	60·25
C^2H^3O	23	.....	17·56	.....	18·34
$C^2H^3CaO^2,2SO^3$	131	.....	100·00	.....	100·00

Uranic salt.—Formed by precipitating sulphomethylate of baryta by 1 At. uranic sulphate, so that the filtrate may not exhibit any turbidity either with sulphuric acid or with a baryta-salt, and leaving it to evaporate in vacuo. The residual syrup, after the lapse of several months, yields crystals which are very deliquescent, and must be dried, first between paper, and then in vacuo. (Péligot, *N. Ann. Chim. Phys.* 12, 560; also *J. pr. Chem.* 35, 152.)

	Dried in vacuo.				Péligot.
U^2O^3	444		56·25		55·8
$2SO^3$	80		31·25		29·9
2 C	12		4·69		4·2
4 H	4		1·56		1·6
2 O	16		6·25		8·5
$C^2H^3(U^2O^2)O^2,2SO^3$ + Aq.	556		100·00		100·0

$= U^2O^3,SO^3 + C^2HO,SO^3 + Aq.$

Lead-salt.—Generally crystallizes in long prisms; sometimes also in tables, which perhaps contain 2 At. water. Easily decomposed by heat into sulphate of lead and sulphate of methyl. The prisms, when dried over oil of vitriol, give off 1 At. water. (Kane.)

	Crystallized in prisms.				Kane.
PbO	112		50·00		49·76
$2SO^3$	80		35·72		35·93
C^2H^2O	23		10·27		9·81
Aq	9		4·01		4·50
$C^2H^3PbO^2,2SO^3$	224		100·00		100·00

Sulphomethylic acid is much less soluble in alcohol than in water.

Besides the baryta-salt above described, there exists also another isomeric with it, and called *Isomeric sulphomethylate of baryta.* According to Dumas & Péligot (*Ann. Chim. Phys.* 61, 199), this salt is obtained by passing the vapour of anhydrous sulphuric acid into anhydrous wood-spirit, diluting the liquid with water, saturating with baryta-water, precipitating the excess of baryta by passing carbonic acid into the liquid, and leaving the filtrate to evaporate at ordinary temperatures.

Very long, thin prisms, apparently rhombic.

	Dried in vacuo.				
BaO,SO^3	116·6		64·92		64·70
SO^3	40·0		22·27		
2 C	12·0		6·68		6·95
3 H	3·0		1·67		1·75
O	8·0		4·46		
$C^2H^3BaO^2,2SO^3$	179·6		100·00		

Sulphamethylane. $C^2H^3Ad,2SO^3$.

Dumas & Péligot (1835). *Ann. Chim. Phys.* 58, 59; also *Ann. Pharm.* 15, 45.

Schwefel-Formamester.

Formed by adding methylic sulphate to aqueous ammonia, gradually and with agitation, because the solution is attended with great evolution of heat, and leaving the solution to evaporate to the crystallizing point in vacuo over oil of vitriol (p. 305).

Large, transparent and colourless tables, which are extremely deliquescent, but may be restored to the crystalline form by drying in vacuo. (Dumas & Péligot).

	Probable Composition.		
2 C	12	.....	10·81
5 H	5	.....	4·50
N	14	.....	12·61
2 SO^3	80	.....	72·08
$C^2H^3Ad,2SO^3$	111	.....	100·00

For Laurent's views of the constitution of this compound vid. *Revue scientif.* 14, 327; 19, 149.

Methylic Nitrate. C^2H^3O,NO^5.

Dumas & Péligot. *Ann. Chim. Phys.* 58, 37 (1835); also *Ann. Pharm.* 15, 26.

Nitrate of Methyl, Nitrate of Oxide of Methyl, Nitric Methyl-ether; Salpetersaures Methyloxyd, Salpeter-Holznaphtha, Salpeter-Formester; Azotate de methylène, Nitrate de methylène.

When nitric acid is heated with wood-spirit, this compound is formed in small quantity, and only towards the end of the distillation. 2 parts of pounded nitre are distilled in a capacious retort with a recently prepared mixture of 5 pts. wood-spirit and 10 oil of vitriol. As the mixture becomes hot, the distillation proceeds without application of heat from without. The distillate is collected in a receiver, containing solution of common salt and surrounded with a frigorific mixture, and provided with a tubulus to convey the uncondensed gases into the chimney. The methylic nitrate, which sinks to the bottom of the receiver, is separated mechanically from the supernatant aqueous fluid, and several times rectified in the water-bath over a mixture of chloride of calcium and oxide of lead. But the resulting liquid, which amounts to 0·5 of the wood-spirit used, has not a constant boiling point, and is therefore a mixture; it begins to boil at 160°, yielding a distillate which smells of hydrocyanic acid, and probably, therefore, consists of methylic formiate; it is not till the temperature rises to 66°, that methylic nitrate passes over in a state of comparative purity.

Colourless liquid, of sp. gr. 1·182 at 20°; boils at 66°, and yields a vapour whose density is 2·640. Has a faint ethereal smell, and is perfectly neutral.

			Dumas & Péligot.		Vol.	Density.
2 C	12	15·58	18·34	C-vapour	2	0·8320
3 H	3	3·90	4·42	H-gas	3	0·2079
N	14	18·18	17·53	N-gas	1	0·9706
6 O	48	62·34	59·71	O-gas	3	3·3279
C^2H^3O,NO^5	77	100·00	100·00		2	5·3384
					1	2·6692

As the analysis does not agree well with the calculation, Dumas & Péligot consider it possible, though not very probable, that the compound may be C^2H^3O,NO^4. [Perhaps the liquid was contaminated with methylic nitrite, C^2H^3O,NO^3, a compound not known in the separate state.]

Methylic nitrate, when set on fire, burns fiercely and with a yellow

flame. Its vapour detonates with the greatest violence at a temperature a little below 150°.—On bringing a flaming body to the aperture of a glass bulb filled with the vapour, not only is the bulb shattered to pieces, but likewise a platinum-crucible in which it may be enclosed. Even a cast iron boiler is burst, when a glass flask containing 200 cubic centimetres of the vapour is heated to the temperature at which it explodes. Nevertheless, the compound may be analyzed in the ordinary way with oxide of copper, the decomposition taking place very quickly, but without explosion. The explosion of the vapour produces water, carbonic acid and nitrogen. [There is not oxygen enough for this. Gm.] Methylic nitrate, heated with alcoholic potash, is rapidly decomposed, with separation of crystals of nitre. (Dumas & Péligot).

Methylic Formiate. C^2H^3O,C^2HO^3.

Dumas & Péligot (1835). *Ann. Chim. Phys.* 58, 48; also *Ann. Pharm.* 5, 35.

Formiate of Methyl, Formiate of Oxide of Methyl, Formic Methyl-ether; Ameisensaures Methyloxyd, Ameisen-Formester; Formiate d'oxyde de methyle.

Equal parts of methylic sulphate and formiate of soda are gently heated in a distillatory apparatus. As soon as the action begins, the mass becomes spontaneously heated, and methylic formiate passes over in a nearly pure state into the receiver, which should be well cooled. The methylic formiate, which afterwards passes over at a higher temperature, is contaminated with a little methylic sulphate. The distillate thus obtained is rectified over formiate of soda, and then once by itself in a dry retort. In this manner, a perfectly pure product is obtained. This compound is not obtained by distilling wood-spirit and formiate of soda with oil of vitriol.

Transparent and colourless liquid, lighter than water, very volatile, and having an ethereal but very pleasant odour. Vapour density=2·084. (Dumas & Péligot). Boils between 36° and 38°; smells like formic ether. (Liebig, *Chim. org.*)

			Dumas & Péligot.		Vol.	Density.
4 C	24	40·00	40·67	C-vapour	4	1·6640
4 H	4	6·67	6·83	H-gas	4	0·2772
4 O	32	53·33	52·50	O-gas	2	2·2186
C^2H^3O,C^2HO^3	60	100·00	100·00		2	4·1598
					1	2·0799

Chloromethylic Formiate. C^2ClH^2O,C^2HO^3.

Dumas & Péligot. *Ann. Chim. Phys.* 58, 52 (1835); also *Ann. Pharm.* 15, 39.

Ameisen-Formester, Oxychlorkohlensaures Methylen, Oxichlorocarbonate de methylène.

Wood-spirit sprinkled into a bottle filled with phosgene gas is decomposed in a few seconds, with great evolution of heat, yielding hydrochloric acid and chloromethylic formiate:

$$C^2H^4O^2 + 2COCl = HCl + C^2H^2ClO,C^2HO^2.$$

If the wood-spirit contains water, the chloromethylic formiate partly separates from the still undecomposed wood-spirit in drops; on the addition of water, it is completely precipitated in the form of an oil, which may be separated from the watery liquid by decantation, and distilled in the water-bath over a very large quantity of chloride of calcium and oxide of lead. By agitating this distillate with chloride of calcium, the last traces of wood-spirit may be removed from it.

Colourless, very fluid oil, heavier than water, very volatile, and having a penetrating odour.

Burns with a green flame. Dissolves with great evolution of heat in aqueous ammonia, producing sal-ammoniac and urethylane, which crystallizes in needles:

$$C^2H^2ClO,C^2HO^2 + 2NH^3 = NH^4Cl + C^4H^5NO^4$$

					Dumas & Péligot.
4 C	24·0	.....	25·42	.....	25·9
3 H	3·0	.....	3·18	.....	3·4
Cl	35·4	.....	37·50	.....	36·6
4 O	32·0	.....	33·90	.....	34·1
C^2H^2ClO,C^2HO^2	94·4	.....	100·00	.....	100·0

Methylal. $C^6H^8O^4$.

Malaguti. *Ann. Chim. Phys.* 70, 390; also *Ann. Pharm.* 32, 55; also *J. pr. Chem.* 18, 67.

To a solution of 120 parts formomethylal in about 176 pts. water, hydrate of potash is added by small portions, each addition causing the liquid to boil up, and the methylal which rises to the surface and forms a distinct stratum, is separated from the alkaline solution.

Transparent and colourless; sp. gr. 0·855 at 18°; boils at 42°; smells like formomethylal. Vapour-density = 2·625.

Chlorine gas passed through methylal acts very slowly upon it, causing rise of temperature and evolution of hydrochloric acid gas, but not till after the lapse of several hours; after a certain interval, however, a violent action is set up. The residue left at the end of the reaction is but small in quantity, because a large portion is lost by evaporation; when washed with water, which dissolves the greater portion, it leaves a liquid, which in 24 hours becomes filled with crystals, and in four weeks is completely converted into sesquichloride of carbon, C^4Cl^6, a large quantity of formic acid having passed into the supernatant water:

$$C^6H^8O^4 + 12Cl = 6HCl + C^2H^2O^4 + C^4Cl^6.$$

[In this change, a compound of the methylene-series appears to be converted into a compound belonging to the ethylene series.]

Methylal, gently heated with moderately dilute nitric acid, gives off nitric oxide gas, and yields a large quantity of formic acid, but neither carbonic acid, carbonic oxide, nor wood-spirit. It acts in a similar manner with bichromate of potash. When briskly agitated with alcoholic

potash, methylal disappears very slowly, taking up 10 At. oxygen [from the air], by which it is converted into formic acid:

$$C^6H^8O^4 + 10O = 3C^2H^2O^4 + 2HO.$$

1 vol. methylal dissolves in 3 vol. water, and may be separated therefrom by saturating the water with potash.—It dissolves in alcohol and ether. (Malaguti.)

		Malaguti.		Vol.	Density.
6 C'	36	47·37	47·86	C-vapour 6	2·4960
8 H	8	10·53	10·53	H-gas 8	0·5544
4 O	32	42·10	41·61	O-gas 2	2·2186
Methylal	76	100·00	100·00	2	5·2690
				1	2·6345

[Methylal is perhaps a copulated compound of a higher order, composed namely of 1 At. methylic formiate with 4 At. wood-spirit, *minus* 4 At. HO:

$$C^4H^4O^4 + 4C^2H^4O^2 - 4HO = C^{12}H^{16}O^8.$$

According to this formula, its vapour will be, not ½-atomic, like that of $C^6H^8O^4$, but ¼-atomic, just as sal-ammoniac vapour, which is ¼-atomic, is formed by the union of hydrochloric acid and ammoniacal *gases*, both of which are ½-atomic. GM.]

According to Liebig (*Chim. org.*), methylal = 2MeO + FoO + Aq = $2C^2H^3,O + 2C^2H,O + HO$.—According to Regnault, it is formed by the union of 3 At. methyl-ether, which have taken up 2O and given off 1HO:

$$3C^2H^3O + 2O - HO = C^6H^8O^4.$$

Formomethylal. $C^6H^{10}O^6$.

KANE. *Phil. Mag. J.* 10, 116; also *Ann. Pharm.* 19, 175.
DUMAS. *Ann. Pharm.* 27, 135.
MALAGUTI. *Ann. Chim. Phys.* 70, 390; also *Ann. Pharm.* 32, 55; also *J. pr. Chem.* 18, 67.

Formal.—First noticed by Gregory, but more completely examined by Kane, Dumas, and Malaguti.

A mixture of 3 pts. oil of vitriol and 3 water is added, after cooling, to 2 pts. of black oxide of manganese and 2 pts. wood-spirit contained in a capacious retort; and the mixture gently heated in the water-bath till it begins to froth up, but no longer, because the heat produced by the reaction of the materials is sufficient for the distillation; towards the end of the operation, however, the heat should be raised to 100°. The distillate, which contains formomethylal, wood-spirit, aldehyde, and a small quantity of lignone, is rectified in the water-bath, the boiling point gradually rising from 40° to 80°; and only that portion is collected which distils over at temperatures not above 60°. The distillate thus obtained consists of formomethylal mixed with a small quantity of aldehyde. (Kane.) [The further purification is not described.]

Transparent, colourless, mobile liquid. Boils at 38° (Kane); at 39·5°...40·5° (Malaguti). Vapour-density = 2·40725 (Kane); = 2·515

(Dumas). Has a pleasant aromatic odour, like that of acetic ether. (Malaguti.)

			Kane.		Dumas.		Malaguti.
8 C	48	45·28	45·84		46·27		45·54
10 H	10	9·44	9·38		9·43		9·58
6 O	48	45·28	44·78		44·30		44·88
	106	100·00	100·00		100·00		100·00

	Vol.	Density.
C-vapour	8	3·3279
H-gas	10	0·6930
O-gas	3	3·3279
	3	7·3488
	1	2·4496

Kane is of opinion that the body which he analyzed still contained aldehyde, and therefore gave too much carbon. The vapour of this compound appears to be ½-atomic, a circumstance of rare occurrence.

Formomethylal mixes with water in all proportions (Kane); 100 measures of it require 170 measures of water to dissolve them. (Malaguti.)

Chlorine yields with formomethylal an oily product, which is rapidly decomposed by water, with production of formic acid. (Dumas.)—Formomethylal is decomposed by potash, yielding wood-spirit and formiate of potash. (Kane, Dumas.)—When 100 pts. formomethylal are mixed with alcohol; hydrate of potash gradually added in quantity sufficient to saturate the alcohol; the mixture left to itself for 5 days, then freed from alcohol by distillation, and mixed with ammonio-nitrate of silver; a quantity of metallic silver is precipitated, from which it may be calculated that only 18 pts. of formic acid, C^2HO^4, have been produced. Now, if formomethylal were constituted as Dumas supposes (*vid. inf.*), the amount of formic acid should be 43·4 per cent. (Malaguti.)—A solution of 100 measures of formomethylal in 176 measures of water gradually mixed with pieces of hydrate of potash, each addition causing the liquid to boil up, is resolved, after complete decomposition, into 70 measures of of methylal, which rise to the top, and a watery, alkaline layer, containing formic acid and wood-spirit.

Hence it appears that formomethylal is a mere mixture of methylal and methylic formiate, which latter is alone decomposed by the potash. The same result is apparent on distilling formomethylal with a thermometer. The distillate, which passes over when the temperature rises to 37°, contains 43·24 per cent. of carbon, and is therefore comparatively rich in methylic formiate; but that which ultimately goes over at 40° contains 40·64 C and 9·74 H, and is therefore richer in methylal. (Malaguti.)

According to Kane, formomethylal is a compound of 1 At. methylic ether and 1 At. methyl-aldide, $C^3H^3O^2$ (a compound not known in the separate state); according to Dumas, it is a compound of 3 At. methylene with 3 At. water and 1 At. hypothetically anhydrous formic acid,—or, what comes to the same thing, it is, according to Liebig's earlier view (*Pogg.* 40, 296), a compound of 3 At. methyl-ether and 1 At. hypothetically anhydrous formic acid. Lastly, according to Malaguti, it is a loosely combined mixture of 2 At. methylal with 1 At. methylic formiate, which latter is decomposed when the mixture is treated with potash.

These several views are exhibited in the following table:

According to Kane.	C	H	O	According to Dumas.	C	H	O	According to Malaguti.	C	H	O
1 At. Methyl-ether....	2	3	1	3 At. Methylene	6	6		2 At. Methylal	12	16	8
1 At. Methyl-aldide	2	2	2	3 At. HO		3	3	1 At. Methylic formiate	4	4	4
				1 At. Formic Acid	2	1	3				
Formomethylal	4	5	3		8	10	6		16	20	12

[It may also be a copulated compound of 1 At. methylic formiate and 2 At. wood-spirit, *minus* 2 HO:

$$C^4H^4O^4 + C^4H^8O^4 - 2HO = C^8H^{10}O^6.$$

When 2 At. of this compound are acted upon by potash, only 1 At. of the methylic formiate is decomposed, and the methylal remains: $C^{16}H^{20}O^{12} - C^4H^4O^4 = C^{12}H^{16}O^8$.]

¶ Methylamine. $C^2H^5N = C^2H^3,H^3N = \left.\begin{matrix} H \\ H \\ C^2H^3 \end{matrix}\right\}N.$

Wurtz (1849). *Compt. rend.* 28, 223, and 323, 29, 169; *Instit.* 1849, 100, 257; *Comptes mensuels.* 1849, 120; *J. pr. Chem.* 47, 345; *Pharm. Centr.* 1849, 264; *Chem. Gaz.* 1849, 115; *Ann. Pharm.* 71, 930; *J. pr. Chem.* 48, 238; *Chem. Soc. Qu. J.* 3, 90.—*Jahresber.* 1849, 394.—More fully: *N. Ann. Chim. Phys.* 30, 443; *J. pr. Chem.* 52, 193; abstr. *Ann. Pharm.* 76, 317; *Pharm. Centr.* 1851, 166, 177; *Jahresber.* 1850, 443.

Methylamide, Methyl-ammonia, Methamine, Methyliaque.—Occurs in the *oleum animale Dippelii.* (Anderson.)

Formation. 1. By the action of potash on cyanate or cyanurate of methyl (Wurtz):

$$C^2NO,C^2H^3O + 2(KO,HO) = 2(KO,CO^2) + C^2H^5N.$$

2. By the action of potash on *methyl-urea*, $C^4H^8N^2O^2$ (Wurtz):

$$C^4H^8N^2O^2 + 2(KO,HO) = 2(KO,CO^2) + NH^3 + C^2H^5N.$$

3. Iodide of methylammonium, $H^3(C^2H^3)N,I$, or hydriodate of methylamine, $H^3(C^2H^3)N,HI$, is formed, among other products, by the action of ammonia on iodide of methyl. (Hofmann, *Chem. Soc. Qu. J.* 4, 320.)—4. By the action of caustic alkalis or of chlorine on various natural alkaloids: *a.* Morphine heated to 200° with hydrate of potash yields a distillate containing methylamine. (Wertheim, *Ann. Pharm.* 73, 210; *Chem. Gaz.* 1850, 142.)—*b.* The distillate obtained by heating *Codeine* to 120°...175° with hydrate of potash contains methylamine, together with ammonia and other basic products.—*c.* Hydrochlorate of methylamine is formed by the action of chlorine on *Theobromine.* (Rochleder & Hlasiwetz, *Wien. Acad. Ber.* März, 266; *Jahresber.* 1850, 437.)—*d.* Also, together with a variety of other products, by the action of chlorine on *Caffeine,* (Rochleder, *Ann. Pharm.* 69, 120; *Wien. Acad. Ber.* 1849, Feb. 93; *N. J. Pharm.* 17, 74; *Jahresber.* 1849, 383; also *Wien. Acad. Ber.* 1850, Juli, 96; *Chem. Gaz.* 1851, 102; *Jahresber.* 1850, 434; Wurtz,

N. J. Pharm. 17, 76; *Jahresber.* 1849, 384; *Compt. rend.* 30, 9.)—Rochleder at first supposed that the base thus obtained was composed of C^3H^4N, and gave it the name of *Formyline*. Wurtz, however, showed that it was really methylamine; and Rochleder, on repeating his experiments, came to the same conclusion.

Preparation. Similar to that of ammonia. Hydrochlorate of methylamine (p. 317), perfectly dried, is mixed with twice its weight of quicklime, and the mixture introduced into a long tube closed at one end, in such quantity as to half fill it, the other half being filled with fragments of hydrate of potash. From this tube a gas-delivery tube passes to the mercurial trough. On applying a gentle heat to the tube, beginning at the closed end, the gas is disengaged and may be collected over the mercury. (Wurtz.)

Properties. Colourless gas, having a strong ammoniacal odour. Like ammonia, it turns reddened litmus-paper blue; fumes strongly with hydrochloric acid; combines with its own volume of that gas and with half its volume of carbonic acid gas; is rapidly absorbed by water, and also by charcoal. It is distinguished from ammonia by taking fire when brought in contact with a lighted taper; it then burns with a yellowish flame, producing water, carbonic acid, and nitrogen, mixed, if the combustion be incomplete, with cyanogen and hydrocyanic acid.—Sp. gr. 1·13 at 25°, and 1·08 at 43°. When cooled a few degrees below 0°, it condenses to a very mobile liquid, which does not solidify in a mixture of solid carbonic acid and ether. (Wurtz).

				Vol.		Density.
2 C	12	38·71	C-vapour	2		0·8320
5 H	5	16·13	H-gas	5		0·3465
N	14	45·16	N-gas	1		0·9706
C^2H^5N	31	100·00		2		2·1491
				1		1·0745

May be regarded: (1) as C^2H^3N,H^2, *i. e.*, as a compound of 2H with a nucleus (C^2H^4) in which 1H is replaced by 1N (*a*, p. 186);—(2) as C^2H^3Ad, *i. e.*, as the same nucleus in which 1H is replaced by 1Ad (*b*, p. 186);—(3) as C^2H^3,NH^3, *i. e.*, as ammonia coupled with methylene (*c*, p. 186), which is the view adopted by Dumas, (*Compt. rend.* 29, 303); (4) or finally, as $\left.\begin{matrix} H \\ H \\ C^2H^3 \end{matrix}\right\}N$, *i. e.*, as ammonia in which 1 At. H is replaced by 1 At. methyl = C^2H^3 (Wurtz, Hofmann). *Compare* pp. 16, 17, and 186.

Decompositions. 1. Methylamine passed through a red-hot porcelain tube, filled with fragments of porcelain, is completely decomposed into free hydrogen, marsh-gas, ammonia, and hydrocyanic acid:

$$3C^2H^5N = NH^3,C^2NH + C^2NH + C^2H^4 + 6H.$$

If the gaseous mixture, as it issues from the tube, be passed through water, and then collected in jars over mercury, the water acquires an alkaline reaction, and is found to contain hydrocyanate of ammonia; and the gas in the jars consists, in 100 measures, of 13·77 vol. hydrocyanic acid, 71·08 hydrogen, and 14·37 marsh-gas.—2. Four vol. methylamine

exploded with 9 vol. oxygen produce 4 vol. carbonic acid and 2 vol. nitrogen. Now 4 vol. CO^2 contain 4 vol. O; hence 5 vol. O must have been consumed in burning the hydrogen, which must therefore amount to 10 vol.; moreover, 4 vol. CO^2 contain 4 vol. carbon-vapour (II., 93); consequently 4 vol. methylamine-gas contain 4 vol. C, 10 vol. H, and 2 vol. N,—or 2 vol. methylamine contain 2 vol. C, 5 H, and 1 N; and as all these gases are monatomic (I., 53), it follows also that the numbers of atoms of C, H, and N, are to one another as 2 : 5 : 1. Hence, if the gas itself be diatomic, its formula must be C^2H^5N. To obtain complete combustion, it is necessary to mix the gas with 3 times its volume of dry oxygen, and to add to the mixture, according to Regnault's recommendation, a certain quantity of detonating gas, derived from the electrolysis of water, also perfectly dry. (Wurtz, *N. Ann. Chim. Phys.* 30, 451.).—*3.* Potassium heated in the gas decomposes it completely, yielding free hydrogen and cyanide of potassium:

$$C^2H^5N + K = C^2NK + 5H,$$

31·5 vol. methylamine yielding 81·5 vol. pure hydrogen, numbers which are nearly in the ratio of 2 : 5. The action, however, exhibits two stages. At first, while the heat is moderate, the volume of gas increases but little, and the residue probably contains $C^2(H^4K)N$, a compound analogous to amide of potassium; and this at a higher temperature is resolved into hydrogen and cyanide of potassium, the latter decomposition being accompanied by the considerable increase in volume which is observed. (Wurtz.)

Combinations.—Aqueous Solution.—Methylamine is the most soluble in water of all known gases. Water at 25° absorbs 959 times, and at 12·5°, 1150 times its volume of the gas.—The solution is prepared by distilling cyanurate of methyl with potash-ley, (p. 313). The liquids are heated together in a flask surmounted by a worm-tube, which serves to condense the aqueous vapour, and separate it from the gaseous methylamine; the gas then passes over into a receiver containing a small quantity of pure water. The complete decomposition of the cyanurate of methyl is a very long operation. It may, however, be accelerated by previously fusing the ether with solid hydrate of potash moistened with a small quantity of water.

The solution has the powerful odour of the gas, and is extremely caustic; it gives off the gas when boiled. It is decomposed by iodine, bromine, and chlorine. Iodine added to it, not in excess, forms hydriodate of methylamine which dissolves, and *Diniodomethylamine*, $C^2(H^3I^2)N$, which remains undissolved:

$$3C^2H^5N + 4I = C^2(H^3I^2)\,N + 2\,(C^2H^5N,HI).$$

Bromine and chlorine appear to act in a similar manner.

The action of aqueous methylamine on metallic salts is, for the most part, similar to that of ammonia. The salts of magnesia, manganese, iron, bismuth, chromium, uranium, and tin, are precipitated by methylamine in the same manner as by ammonia. With zinc-salts, methylamine forms a white precipitate, soluble in a large excess of the reagent. With copper-salts, a bluish white precipitate, easily soluble in excess, and forming a deep blue solution. With cadmium-salts, a white precipitate, insoluble in excess. With nickel and cobalt salts, also, it forms precipitates insoluble in excess. These last three reactions differ from those produced by ammonia. Acetate of lead is scarcely clouded by

methylamine, but the nitrate is completely precipitated. With mercurous salts, methylamine, like ammonia, forms a black precipitate;—with corrosive sublimate, a white, flocculent precipitate, insoluble in excess.—Nitrate of silver is completely precipitated by methylamine; and the oxide, whether precipitated by the alkaloid itself or by potash, dissolves readily in excess of the former. The solution, abandoned to spontaneous evaporation, deposits a black substance, which contains carbon, hydrogen, nitrogen, and silver, and is probably the analogue of fulminating silver; but does not explode either by heat or by percussion. Chloride of silver is also dissolved by aqueous methylamine. With terchloride of gold, methylamine forms a brownish yellow precipitate, which dissolves readily in an excess of the precipitant, forming an orange-red solution. A concentrated solution of bichloride of platinum forms, with methylamine, a crystalline deposit, consisting of chloroplatinate of methylamine, in the form of orange-yellow scales. The formation of this precipitate is prevented, even by slight dilution. (Wurtz.)

Carbonate of Methylamine.—Gaseous methylamine unites with half its volume of carbonic acid gas, forming a white solid body, analogous to the anhydrous carbonate of ammonia (II., 430, *a*).—The salt is prepared by distilling the fused hydrochlorate with carbonate of lime. The product of the distillation is a very thick liquid, having a quantity of solid matter in the middle: the liquid is a highly concentrated solution of carbonate of methylamine; the solid is the anhydrous carbonate. On gently heating the contents of the receiver, the anhydrous carbonate partly dissolves and partly volatilizes. The liquid portion, as it cools, deposits crystals of the hydrated salt, which is highly deliquescent, and volatilizes even at ordinary temperatures. It is, however, very difficult to obtain either the anhydrous or the hydrated salt in a state of purity. The substance analyzed by Wurtz appears to have been a mixture of the two.

Anhydrous.			Wurtz.		*Hydrated.*		
3 C	18	33·96	30·8	32·1	3 C	18	29·03
5 H	5	9·43	9·4	9·6	6 H	6	9·67
N	14	26·43			N	14	38·71
2 O	16	30·18			3 O	24	22·59
C^3H^5N,CO^2	53	100·00			C^3H^5N,CO^2H	62	100·00

The so-called anhydrous carbonate is analogous to the compound which Rose calls carbonate of ammon. (II. 430.)

Sulphate.—Very soluble in water; insoluble in alcohol; does not crystallize. Evaporated with cyanate of potash, it yields methyl-urea, $C^4H^8N^2O^2$. (Wurtz.)

Hydriodate.—C^3H^5N,HI.—Obtained by the action of iodine on methylamine dissolved in water (p. 315); also by saturating the solution with hydriodic acid.—Colourless plates, which turn brown on exposure to the air; they are very deliquescent, and dissolve very readily in water and alcohol. (Wurtz.)

Hydrobromate.—Obtained by the action of bromine on the aqueous solution of methylamine. Very soluble in water and in alcohol. From the alcoholic solution it crystallizes in large, brilliant plates, which have an unctuous aspect, and are very deliquescent. (Wurtz.)

				Wurtz.
2 C	12	10·71		10·89
6 H	6	5·35		5·65
N	14	12·51		
Br	80	71·43		
C^2H^5N,HBr	112	100·00		

Hydrochlorate.—Gaseous methylamine unites with its own volume of hydrochloric acid gas, forming a white, solid salt, which adheres like sal-ammoniac to the sides of the vessel.—The salt is prepared by saturating aqueous methylamine with hydrochloric acid, and evaporating to dryness. The residue dissolves easily in boiling alcohol, and crystallizes on cooling in fine, large laminæ, which, at the moment of their formation, appear iridescent by reflected light. Deliquescent; does not fuse till heated above 100°. Heated in an open vessel to a very high temperature, it volatilizes in very dense vapours, which condense in a white powder on the surface of cold bodies. (Wurtz.)

				Wurtz.
2 C	12·0	17·77		17·45
6 H	6·0	8·88		8·78
N	14·0	20·83		
Cl	35·4	52·52		52·45
C^2H^5N,HCl	67·4	100·00		

When a solution of this salt, either in water or in alcohol, is treated with amalgam of potassium, hydrogen is evolved, and the liquid becomes alkaline. Wurtz has not yet succeeded in obtaining by this reaction an amalgam of methylammonium corresponding to the *ammoniacal amalgam* (I., 457). Neither is such a compound produced by placing mercury in a cavity in a lump of hydrochlorate of methylamine, and connecting it with the voltaic battery. (Wurtz.)

Nitrate.—Formed by saturating aqueous methylamine with nitric acid. The solution, when evaporated, yields beautiful, right rhomboidal prisms, very much elongated, and closely resembling the crystals of nitrate of ammonia. They are deliquescent, and dissolve very readily in water and alcohol. They are decomposed by distillation, yielding gaseous products, and drops of an oily liquid, insoluble in water. (Wurtz.)

				Wurtz.
2 C	12	12·77		12·22
6 H	6	6·38		6·44
2 N	28	29·79		
6 O	48	51·06		
C^2H^5N,HO,NO^5	94	100·00		

Chloromercurate of Methylamine.—$C^2H^5N,HCl,HgCl$.—Formed by evaporating a mixture of 1 At. hydrochlorate of methylamine and 1 At. corrosive sublimate. The solution, when highly concentrated, yields bulky crystals of the double salt. (Wurtz.)

Chloro-aurate.—On mixing a solution of hydrochlorate of methylamine with a solution of chloride of gold, no precipitate is formed; but on evaporating till the liquid becomes very concentrated and then leaving it to

cool, the double salt is obtained in splendid golden-yellow needles, which are soluble in water, alcohol, and ether. (Wurtz.)

				Wurtz.
2 C	12·0	3·22		3·03
6 H	6·0	1·61		1·60
4 Cl	141·6	38·00		37·82
Au	199·0	53·41		
N	14·0	3·76		
$C^2H^5N,HCl,AuCl^3$	372·6	100·00		

Chloroplatinate.—Beautiful golden-yellow scales, which are soluble in boiling water and recrystallize on cooling. Insoluble in alcohol. When heated they blacken, emitting very copious fumes, and leaving a residue of platinum mixed with charcoal, which burns in the air. (Wurtz.)

				Wurtz.
2 C	12·0	5·06		5·15
6 H	6·0	2·53		2·65
3 Cl	106·2	44·87		44·45
Pt	99·0	41·64		41·37
N	14·0	5·90		
$C^2H^5N,HCl,PtCl^2$	237·2	100·00		

Compounds of Methylamine with Protochloride of Platinum.—*a.* $2(PtCl,C^2H^5N) = 2C^2H^5N,PtCl + PtCl$.—When protochloride of platinum, suspended in a small quantity of water, is treated with a concentrated solution of methylamine, heat is evolved, and the olive-brown compound is converted into a chrome-green powder. (Wurtz.)

				Wurtz.
4 C	24·0	7·26		
10 H	10·0	3·02		
2 Pt	198·0	59·87		59·75
2 Cl	70·8	21·39		
2 N	28·0	8·46		
$2(PtCl,C^2H^5N)$	330·8	100·00		

Analogous to Magnus's green compound, $2NH^3,PtCl + PtCl$:—May also be regarded, according to Gerhardt's nomenclature and formulæ, as *Chloroplatinate of Diplatoso-methylamine*, $PtCl^2H,N^2(C^4H^9)Pt$ (*vid.* VI., 304.)

b. $C^4H^9PtN^2,HCl = 2(C^2H^5N),PtCl$.—When the compound *a* is introduced, together with an excess of methylamine, into a small, narrow-necked flask, the flask sealed, and then heated for a while in the water-bath, the precipitate gradually dissolves, and at the end of the process, there remains nothing but a small quantity of a black insoluble powder. The point of the flask is then broken, the excess of methylamine distilled off by heat, and the remaining liquid filtered. The nearly colourless solution thus obtained is evaporated to a syrupy consistence, and ultimately solidifies in a crystalline mass. The crystals are separated from the adhering mother-liquor by pressure between paper, then purified by several crystallizations from water, and finally from alcohol, in which they dissolve less readily than in water. (Wurtz.)

				Wurtz.
4 C	24·0	....	12·22	12·32
10 H	10·0	....	5·09	5·11
Pt	99·0	....	50·41	50·00
Cl	35·4	....	18·02	
2 N	28·0	....	14·26	
$2(C^2H^5N),PtCl$	196·4	....	100·00	

This compound is analogous to Reiset's first chloride, $2NH^3,PtCl$ (VI., 300).—According to Gerhardt's notation, it may be regarded as the *Hydrochlorate of Diplatoso-methylamine*, $N^2(C^4H^3)Pt,HCl$.—Wurtz's formula $\left.\begin{matrix}C^2H^5N \\ C^2(H^4Pt)N\end{matrix}\right\}$ HCl is scarcely admissible, inasmuch as it implies that hydrochloric acid can act as a bibasic acid.

¶ Diniodo-methylamine. $C^2(H^2I^2)N$.

WURTZ. *N. Ann. Chim. Phys.* 30, 455.

Formed by the action of iodine on the aqueous solution of methylamine (p. 315).

Garnet-coloured powder, which dissolves in alcohol, but appears to be decomposed by that liquid.

				Wurtz.
2 C	12	....	4·27	4·12
3 H	3	....	1·06	1.57
2 I	252	....	89·32	89·57
N	14	....	5·35	
$C^2\left\{\begin{matrix}H^2 \\ I^2\end{matrix}\right\}N$	281	....	100·00	

This compound is decomposed by heat, but does not explode like the iodide of nitrogen. It is also decomposed by potash, with formation of iodide of potassium, a volatile product having a very penetrating odour, and a slight insoluble residue consisting of a yellow flocculent matter, not yet examined; Wurtz has, however, ascertained that this residue does not consist of iodoform. (Wurtz.)

¶ Dimethylamine. $C^4H^7N = (C^2H^3)^2,H^2N = (C^2H^3)^2,HN$.

This compound has been but little studied. It is formed as a hydriodate (or iodide of dimethylium) by the action of ammonia on iodide of methyl (pp. 179, 321). The hydriodate distilled with caustic potash yields the alkali in the free state. (Hofmann, *Chem. Soc. Qu. J.* 4, 322.)

	Calculation.		
4 C	24	.....	53·33
7 H	7	.....	15·56
N	14	.....	31·11
C^4H^7N	45	.....	100·00

¶ Trimethylamine. $C^6H^9N = (C^2H^2)^3,H^3N = (C^2H^3)^3N$.

Occurs in herring-brine (Hofmann, *Chem. Soc. Qu. J.* 5, 288; *Ann. Pharm.* 83, 116).—The hydriodate is formed by the action of ammonia on iodide of methyl; and on distilling this compound with potash, the alkali is obtained in the free state. (Hofmann, *Chem. Soc. Qu. J.* 4, 322).

	Calculation.		
6 C	36	.....	61·02
9 H	9	.....	15·25
N	14	.....	23·73
C^6H^9N	59	.....	100·00

¶ Tetramethylium. $C^8H^{12}N = (C^2H^3)^4,H^4N = (C^2H^3)^4,N$.

Hofmann. *Phil. Trans.* 1850, 93; *Chem. Soc. Qu. J.* 5, 320; *Ann. Pharm.* 79, 11; *N. Ann. Chim. Phys.* 33, 108.

Syn. *Tetramethylammonium.*

Obtained in the form of an iodide by the action of ammonia on the iodide of methyl.

Not known in the separate state (p. 17).

	Calculation.		
8 C	48	.....	16·22
12 H	12	.....	64·86
N	14	.....	18·92
$(C^2H^3)^4N$	74	.....	100·00

Hydrated Oxide.—$(C^2H^3)^4NO,HO$.—Obtained by digesting oxide of silver in the aqueous solution of the iodide:

$$(C^2H^3)^4\,N,I + AgO + HO = AgI + (C^2H^3)^4\,NO,HO.$$

On filtering to separate the iodide of silver, a strongly alkaline solution is obtained, which when evaporated in vacuo over sulphuric acid, yields a white crystalline mass, resembling hydrate of potash, and absorbing water and carbonic acid with avidity (p. 17).

When heated, it intumesces strongly, and is completely volatilized, yielding a strongly alkaline distillate. According to the decomposition-products obtained with other bodies of similar composition—the hydrated oxide of tetrethylium, for example—it might be expected to yield trimethylamine and methylene, C^2H^2; but it appears to be decomposed in a different manner, as not a trace of permanent gas is given off (*vid.* p. 180.)

Neutralized with acids, it yields crystallizable salts. The sulphate, oxalate, nitrate, and hydrochlorate have been prepared. The nitrate crystallizes in long shining needles. (Hofmann.)

Iodide.—Iodide of methyl heated in a sealed tube with strong aqueous ammonia, is quickly dissolved, the completion of the action being indicated

by the appearance of a yellow colour in the solution. On opening the tube, the solution is found to be strongly acid, and contains five different iodides, viz., the iodides of ammonium, H^4N; methylium, $(H^3,C^2H^3)N$ [or $(H^2,Me)N$]; dimethylium, $(H^2,Me^2)N$; trimethylium, $(H,Me^3)N$; and tetramethylium, Me^4N. The first and last of these compounds are produced in abundance, the second in smaller quantity, and the third and fourth in very small quantity. The action takes place even at ordinary temperatures, but less quickly, several days being required to complete it. If an alcoholic solution of ammonia be used, the action is completed in a few hours, even at ordinary temperatures.—If the iodide of methyl is in excess, the hot solution, as it cools, deposits crystals of the iodide of tetramethylium, which may be purified by washing with cold water, and recrystallization from hot water.

Hard, flat needles, of dazzling whiteness; sparingly soluble in cold, more soluble in boiling water. The solution is neutral, and has an extremely bitter taste. The crystals are nearly insoluble in alcohol, quite insoluble in ether, sparingly soluble in an alkaline liquid. (Hofmann.)

				Hofmann.
8 C	48	....	24	
12 H	12	....	6	
N	14	....	7	
I	126	....	63	..... 62·94
$(C^2H^3)^4N,I$	200	....	100	

Chloroplatinate.—Formed by mixing the solution of the hydrochlorate with bichloride of platinum. Crystallizes in well-defined octohedrons, of a deep orange-yellow colour. (Hofmann.)

				Hofmann.
8 C	48·0	....	17·18	
12 H	12·0	....	4·29	
3 Cl	106·2	....	38·07	
N	14·0	....	5·00	
Pt	99·0	....	35·46	..... 35·21
$(C^2H^3)^4NCl,PtCl^2$	279·2	....	100·00	

When this salt is recrystallized, the proportion of platinum is found to diminish, in consequence of a decomposition which takes place by the action of boiling water. A similar decomposition has been observed in the platinum-salts of the other ammonium-bases. (Hofmann.)

¶. Stibmethyl. $C^6H^9Sb = (C^2H^3)^3,H^3Sb = (C^2H^3)^3Sb$.

LANDOLT. *Ann. Pharm.* 78, 91; *J. pr. Chem.* 52, 385; *Instit.* 1851, 142; abstr. *Pharm. Centr.* 1851, 233; *N. Ann. Chim. Phys.* 34, 226; *N. J. Pharm.* 20, 35; *Jahresber.* 1851, 501; *Chem. Soc. Qu. J.* 5, 67.

This compound is formed by the action of iodide of methyl on antimonide of potassium (p. 286). A small short-necked flask, having a capacity of 3 or 4 ounces, is about two-thirds filled with a mixture of antimonide of potassium (obtained by igniting 5 parts of crude tartar with 4 of antimony, and containing 12 per cent. of potassium) and quartz-sand, the sand being used to diminish the intensity of the action. Pure anhydrous iodide of methyl is then introduced, in quantity sufficient to moisten the mixture, whereupon a violent action takes place, and the

excess of iodide of methyl volatilizes. As soon as this action ceases, the flask is connected by a tube with a receiver filled with carbonic acid, and enclosed within a larger vessel, through which carbonic acid is passed during the whole operation, to exclude the air. The receiver also contains a small quantity of antimonide of potassium. A gentle heat is then applied, and the stibmethyl distils over. The operation is repeated with fresh quantities of material, and the whole distillate is rectified in an atmosphere of carbonic acid, the vessel formerly used as the receiver now serving as a distilling vessel. (Landolt.)—The apparatus used in this process is the same as that used by Löwig and Schweizer in the preparation of *stibethyl* (*q. v.*)

Colourless, heavy liquid, having a peculiar odour; insoluble in water, sparingly soluble in alcohol, readily in ether. When exposed to the air, it gives off thick white fumes, and takes fire, burning with a white flame, and with separation of metallic antimony. (Landolt.)

	Calculation.		
6 C	36	.....	20·69
9 H	9	.....	5·17
Sb	129	.....	74·14
Me^3Sb	174	.....	100·00

Stibmethyl unites with 2 At. oxygen, forming a base Me^3SbO^2, which saturates 2 At. of acid; *e. g.*, *sulphate of stibmethyl* = $Me^3SbO^2, 2SO^3$; *nitrate* = $Me^3SbO^2, 2NO^5$, &c. It likewise unites with 2 At. S, I, Br, Cl, &c.; thus chloride of stibmethyl = Me^3Sb, Cl^2. These compounds are in all essential particulars similar to the corresponding compounds of stibethyl, which will be described hereafter. (Landolt.)

¶ Stibmethylium. $(C^2H^2)^4, H^4Sb = C^8H^{12}Sb = (C^2H^2)^4Sb = Me^4Sb$.

LANDOLT. *Ann. Pharm.* 78, 91; abstr. *Jahresber.* 1851, 501; *Chem. Soc. Qu. J.* 5, 67;—further and more fully: *Mittheil-ungen der Naturforsch. Gesellsh. in Zürich*, Nos. 72, 73, 74; *Chem. Gaz.* 1852, 381, 404.

Obtained in the form of an iodide, by the action of iodide of methyl on stibmethyl (*vid.* p. 326).

$$Me^3Sb + MeI = Me^4SbI.$$

The iodide is decomposed by distillation with antimonide of potassium, and also by electrolysis; but it is not yet distinctly ascertained whether these decompositions yield stibmethylium in the free state.—1. When finely pulverized iodide of stibmethylium is distilled with excess of pulverized antimonide of potassium and quartz-sand in an apparatus filled with carbonic acid, an oily slightly yellow liquid is obtained, which is heavier than water, has the odour of stibmethyl, and takes fire on coming in contact with the air, giving off a white vapour, which condenses to a white powder slightly soluble in water; the solution has a faint alkaline reaction. The quantity obtained was not sufficient for analysis.—2. When an aqueous solution of the iodide is subjected to the action of the electric current, iodine and a small quantity of oxygen (from decomposition of water) are separated at the positive pole, while at the

negative pole, the liquid becomes milky, acquires an alkaline reaction, and gives off a gas equal in volume to ten times the oxygen evolved at the positive pole. This gas contains antimony, has the odour of stibmethyl, and takes fire spontaneously in the air, producing a white smoke; when shaken up with alchoholic solution of iodine, it diminishes in volume and decolorizes the liquid. These characters seem to show that the gas is stibmethylium, although it differs in physical character from the product obtained by (1.) (Landolt). [It might perhaps have liquefied if proper means had been taken to condense it.]

	Calculation.		
8 C	48	.....	25·40
12 H	12	.....	6·35
Sb	129	.....	68·25
$(C^2H^3)^4Sb$	189	.....	100·00

Hydrated Oxide. — $(C^2H^3)^4SbO,HO$. — Obtained by agitating an aqueous solution of the iodide with recently precipitated oxide of silver, filtering from the iodide of silver, and evaporating the filtrate in vacuo over sulphuric acid:

$$(C^2H^3)^4\,Sb,I + AgO + HO = AgI + (C^2H^3)^4\,SbO,HO.$$

White, crystalline mass, which feels soapy between the fingers, is highly caustic, and dissolves readily in water and alcohol, but is insoluble in ether. In the state of aqueous solution, it is slightly volatile, and forms white fumes when a glass rod, moistened with hydrochloric acid, is held over it; but the solution when evaporated over the water-bath yields the original quantity with scarcely any loss. When the solid hydrate is suddenly heated in a test-tube, it gives off vapours which take fire on coming in contact with the air, and deposit metallic antimony; but when carefully heated, it sublimes undecomposed.

The aqueous solution has an alkaline taste and odour, and instantly turns reddened litmus paper blue. In all its chemical relations, it exhibits the closest resemblance to caustic potash. When evaporated in an open vessel, it absorbs carbonic acid, and then effervesces strongly with acids; but on the addition of lime-water, carbonate of lime is precipitated, and the pure base is again found in the solution. It expels ammonia from ammoniacal salts, even in the cold, and separates baryta from iodide of barium. Lime and oxide of lead are immediately precipitated by the solution of this base. With zinc-salts it forms a white precipitate, soluble in excess; with copper-salts, a precipitate insoluble in excess; with mercurous, mercuric, and silver salts, it gives the same reactions as potash; with chloride of platinum, it forms a yellow precipitate, resembling the chloroplatinate of potassium.—The aqueous solution, boiled with sulphur, forms a yellow liquid, which, when mixed with dilute acids, yields a precipitate of sulphur, and gives off sulphuretted hydrogen. In short, this body bears so close a resemblance to potash, as to be quite undistinguishable from it by merely qualitative tests. It is also analogous to the hydrated oxides of tetrethylium, tetramethylium, &c.

With acids, the oxide of stibmethylium forms both neutral and acid salts, which, as far as observations have hitherto extended, closely resemble the corresponding potash-salts, and are isomorphous with them. They all taste bitter. They are formed in some cases by direct combination, in others by double decomposition. (Landolt.)

Carbonates. a. Neutral Carbonate. Me^4SbO,CO^2, or Me^4SB,CO^2?—Obtained by decomposing a solution of the iodide with recently precipitated carbonate of silver. The filtered liquid evaporated over the water-bath leaves an indistinctly crystallized, somewhat yellowish, transparent mass, which deliquesces very readily in the air, exhibits an alkaline reaction, dissolves very easily in water and in alcohol, but very slowly in ether. This compound is very instable, beginning to smell of stibmethyl, as soon as it is formed. When heated, it gives off white fumes, which take fire spontaneously in the air. Does not appear to contain water of crystallization. (Landolt.)

b. Acid Carbonate. $Me^4SbO,HO,2CO^2=(Me^4Sb,H),2CO^2$?—Formed by passing carbonic acid through a solution of the oxide or of the neutral carbonate, and evaporating.—Crystallizes with difficulty in small needles arranged in stars; deliquescent, easily soluble in water and alcohol, insoluble in ether. Has an alkaline reaction and bitter taste. In the solid form it soon decomposes, like the neutral carbonate. The aqueous solution evolves carbonic acid when heated, and does not precipitate magnesia-salts.—The great facility with which these carbonates decompose, rendered it impossible to analyze them. (Landolt.)

Sulphide. Me^4SbS.—Prepared, like monosulphide of potassium, by dividing an aqueous or alcoholic solution of oxide of stibmethylium into two equal parts, saturating the one completely with sulphuretted hydrogen, and then adding the other portion. The resulting solution, when rapidly evaporated in a retort, leaves the sulphide in the form of an amorphous green powder, which smells like mercaptan, dissolves readily in water and alcohol, but is insoluble in ether. The solutions are colourless, and yield black precipitates with nitrate of silver and acetate of lead. On distilling the aqueous or alcoholic solution, part of the sulphide passes over undecomposed; hence it appears to be somewhat volatile. (Landolt.)

				Landolt.
8 C	48	....	23·41	
12 H	12	....	5·85	
Sb	129	....	62·93	
S	16	....	7·81	..... 8·86
$(C^2H^3)^4SbS$	205	....	100·00	

The excess in the determination of the sulphur arises from the facility with which the compound becomes oxidized. The sulphur was determined by precipitating with acetate of lead, oxidizing the sulphide of lead with nitric acid, &c.

Sulphide of stibmethylium heated in a tube, first melts, and then decomposes, evolving vapours which take fire spontaneously, and leaving a hard yellowish mass of sulphide of antimony. In contact with the air, it oxidizes very rapidly, changing to a yellow powder, which gradually becomes white, and is then perfectly soluble in alcohol, but not in water. The alcoholic solution gives, with nitrate of silver, a precipitate which is brown at first, but afterwards turns black; ether changes it to a soft greasy mass, but does not dissolve it. When the white product of oxidation is heated in platinum foil, it first acquires a dark green colour, which disappears on cooling; but if the heat be further increased, the substance becomes white again, and then takes fire. (Landolt.)

A solution of oxide of stibmethylium boiled with sulphur yields milk of sulphur on the addition of an acid; hence it is probable that higher sulphides of stibmethylium may be formed. (Landolt.)

Sulphates. a. Neutral Sulphate. $Me^4SbO,SO^3=Me^4Sb,SO^4$.—Obtained, 1, by adding a hot solution of sulphate of silver to aqueous iodide of stibmethylium as long as any precipitate of iodide of silver is formed. [In Landolt's first memoir on stibmethylium (*Ann. Pharm.* 78, 84), this method is said to yield the acid sulphate.] On evaporating the filtered liquid over the water-bath, colourless crystals are obtained, which may be pressed between paper and dried in the air. (*Chem. Gaz.* 1852, 408.)—2. By saturating a concentrated solution of the acid salt *b* with oxide of stibmethylium, and mixing the aqueous solution with alcohol and ether; the neutral salt then separates in oily drops, which after a while assume the solid form. (*Ann. Pharm.* 78, 95.)—The crystals, which appear to be rhombic, contain 15·42 per cent. (5 At.) water of crystallization, which they give off at 100°. Placed over sulphuric acid, they lose part of their water, and fall to a white powder.—The crystals dissolve very readily in water; the anhydrous salt becomes strongly heated when water is poured upon it. The salt is also soluble in alcohol, but insoluble in ether. Its taste is saline and bitter. (Landolt.)

When this salt is heated above 100° in a chloride of zinc bath, it begins to decompose slowly at 120° to 130°, emitting an odour of stibmethyl; at 150° it melts, and at 190° suffers complete decomposition, attended with evolution of light and heat. By long exposure to a temperature of 100° it suffers gradual decomposition. (Landolt.)

Anhydrous.			Landolt.	*Crystallized.*			Landolt.
8 C	48	20·25		8 C	48	17·02	
12 H	12	5·06		12 H	12	4·25	
Sb	129	54·43		Sb	129	45·75	
O	8	3·38		O	8	2·83	
SO^3	40	16·88	16·94	SO^3	40	14·19	
				5 HO	45	15·96	15·42
$(C^2H^3)^4Sb,SO^4$	237	100·00		+ 5Aq	282	100·00	

Bisulphate. $Me^4SbO,HO,2SO^3=\left.\begin{matrix}Me^4Sb\\H\end{matrix}\right\}2SO^4$.—Obtained by adding 1 At. oil of vitriol to an aqueous solution of 1 At. of the neutral sulphate. After several crystallizations, beautiful, hard, transparent crystals are obtained, some of which are four-sided tablets with obliquely truncated edges. Dissolves very readily in water, less easily in alcohol, and is nearly insoluble in ether. Has a strongly acid taste, and leaves a bitter taste in the mouth. When heated, it behaves exactly like the neutral sulphate. On dissolving it in a small quantity of water, then adding alcohol, precipitating by ether, and repeating these operations several times, the neutral sulphate is at length obtained. In this respect the acid salt behaves exactly like bisulphate of potash. (Landolt.)

			Landolt.
8 C	48	16·78	16·98
13 H	13	4·55	4·43
Sb	129	45·11	
2O	16	5·59	
$2SO^3$	80	27·97	28·08
$(C^2H^3)^4\left.\begin{matrix}Sb\\H\end{matrix}\right\}2SO^4$	286	100·00	

The salt contains no water of crystallization. The basic water (or hydrogen), like that of acid sulphate of potash, is not driven off at 120°.

Iodide. Me^4SbI.—Formed by the action of iodide of methyl on stibmethyl. If, in the preparation of stibmethyl (pp. 321, 322)), the iodide of methyl which distils over at first, and the stibmethyl which passes over when the temperature is raised, are collected in the same receiver, a slight ebullition takes place, and the liquid mixture solidifies after a while into a perfectly white, crystalline mass. This is dissolved in warm water, the excess of iodide of methyl separated, and the solution set aside to evaporate slowly over the water-bath; the iodide of stibmethylium separates in crystals.

The crystals belong to the hexagonal system. They are remarkably beautiful, large, six-sided tables, usually scalariform, and from 10 to 15 millimetres in diameter; the terminal faces are plane, and the lateral edges intersect one another at angles of 120°. The crystals contain water mechanically enclosed, and consequently decrepitate when heated. They dissolve in 3·3 pts. of water at 23°, and are likewise easily soluble in alcohol, but dissolve very slowly in ether.

Iodide of stibmethylium heated in a test-tube first falls to powder, and at 200° begins to decompose, disappearing gradually, and evolving thick white fumes, which have the odour of stibmethyl. The vapour thus evolved is partly deposited as a coating on the inside of the tube; but the greater portion reaches the mouth, where it takes fire spontaneously, forming rings of smoke like phosphuretted hydrogen. Boiling water dissolves but a small portion of the deposit in the tube. The solution treated with nitrate of silver yields a precipitate consisting of iodide of silver and metallic silver, the latter being doubtless produced by pure stibmethyl or stibmethylium, the former by undecomposed iodide.—The aqueous solution of iodide of stibmethylium is gradually decomposed by repeated evaporation, a small quantity of a yellow insoluble substance (not yet examined) being formed, and the odour of stibmethyl evolved. —(For the decomposition by electrolysis, *vid.* p. 322.) Filtering paper, covered with strong starch-paste, to which iodide of stibmethylium has been added, behaves towards *ozone* exactly in the same manner as paper prepared with iodide of potassium, but is even more sensitive.—Oil of vitriol, bromine, chlorine, and nitric acid, act upon iodide of stibmethylium exactly as upon iodide of potassium; hydrochloric acid decomposes it, with formation of chloride of stibmethylium.—Aqueous solution of iodide of stibmethylium poured upon amalgam of sodium, produces a succession of little explosions, accompanied by appearance of fire, metallic antimony being also separated.—The iodide distilled with excess of antimonide of potassium, yields a yellow oily liquid, which is probably stibmethylium (p. 322). The aqueous solution dissolves a considerable quantity of the yellow modification of mercuric iodide. The red iodide, boiled in the solution, changes into the yellow modification before it dissolves; and, as the liquid cools, a considerable portion of the mercuric iodide separates out, but always in the yellow modification. (Landolt.)

				Landolt (*mean*).
8 C	48	....	15·24	..... 15·54
12 H	12	....	3·81	..... 4·11
Sb	129	....	40·95	..... 39·63
I	126	....	40·00	..... 41·16
$(C^2H^3)^4SbI$	315	....	100·00	

The excess in the iodine arises partly from the compound having been somewhat

decomposed by keeping, and is partly due to the error which always arises in precipitating the iodine of organic compounds with nitrate of silver. (Landolt.)

Bromide. Me^4SbBr.—Obtained by decomposing iodide of stibmethylium with bromide of mercury. On filtering from the iodide of mercury and evaporating, a beautiful salt is obtained, soluble in alcohol and water, but insoluble in ether, and having a saline bitter taste.—This compound, when heated in the air, evolves white vapours, which take fire in the air. Oil of vitriol poured upon it liberates hydrobromic acid; nitric acid separates bromine. With metallic salts, bromide of stibmethylium behaves in the same manner as bromide of potassium. (Landolt.)

				Landolt.
8 C	48	17·84		18·38
12 H	12	4·46		5·05
Sb	129	47·96		47·07
Br	80	29·74		29·40
$(C^2H^3)^4SbBr$	269	100·00		99·90

Chloride. Me^4Sb,Cl.—Obtained by adding a hot solution of corrosive sublimate to aqueous iodide of stibmethylium, as long as a precipitate of iodide of mercury is produced. The filtered liquid evaporated over the water-bath deposits the chloride in white six-sided tables similar to those of the iodide. These crystals are easily soluble in water and alcohol, nearly insoluble in ether; their taste is saline and bitter. This salt intumesces when heated in a tube, and at a higher temperature gradually disappears, giving off white fumes, which take fire spontaneously in the air, and deposit on the cooler part of the tube a white sublimate containing chloride of antimony. (Landolt.)

				Landolt.
8 C	48·0	21·38		
12 H	12·0	5·35		
Sb	129·0	57·46		
Cl	35·4	15·81		15·65
$(C^2H^3)^4SbCl$	224·4	100·00		

Nitrate. $Me^4SbO,NO^5 = Me^4Sb,NO^6$.—Formed by adding nitrate of silver to an aqueous solution of iodide of stibmethylium as long as any precipitate is formed, then filtering and evaporating till the salt crystallizes.—The crystals are anhydrous; their form could not be exactly determined; but when a drop of the aqueous solution was allowed to evaporate on a glass plate placed under the microscope, coarsely radiated forms were observed like those of nitrate of potash.—The salt dissolves readily in water, slowly in alcohol or ether. Its taste is harsh and bitter, not cooling like that of nitre. When heated it gives off white fumes, which immediately take fire; the entire mass then explodes with a large white flame, just like a mixture of nitre and charcoal. The salt is very stable, not being decomposed even by boiling with strong sulphuric acid. (Landolt.)

				Landolt.
8 C	48	19·13		
12 H	12	4·78		
Sb	129	51·39		
O	8	3·19		
NO^5	54	21·51		20·91
$(C^2H^3)^4Sb,NO^6$	251	100·00		

Chloroplatinate. $Me^4SbCl,PtCl^2$.—When bichloride of platinum is added to an aqueous solution of chloride of stibmethylium, a yellow crystalline precipitate is formed, which may be dissolved by boiling with water. On cooling, the double salt separates in small crystals, which may be dried between paper.—This salt forms a beautiful orange-yellow powder. It is the least soluble of all the known compounds of stibmethylium; with respect to solubility in water, it is intermediate between the corresponding potassium and sodium compounds; it imparts a yellow colour to a large quantity of cold water, but does not dissolve completely till boiled. It is quite insoluble in alcohol and ether, very difficult of solution in alkalis, but dissolves more easily in hydrochloric acid. When heated, it turns black, and soon takes fire, leaving an alloy of platinum and antimony fused into globules, from which the latter metal is but imperfectly removed by boiling in aqua-regia. (Landolt.)

				Landolt.		
8 C	48·0	....	12·19			
12 H	12·0	....	3·04			
Sb	129·0	....	32·73			
Pt	99·0	....	25·01	.....	24·75	.... 25·62
3 Cl	106·2	....	27·03			
$(C^2H^2)^4SbCl,PtCl^2$	394·2	...	100·00			

¶ Methyl-bases containing Phosphorus.

P. THENARD.—*vid. Memoirs cited on page* 176.

These compounds are formed by the action of chloride of methyl on phosphide of calcium at a high temperature.

a. Biphosphomethyl. $C^2H^3,P^2=MeP^2$.—Phosphobimethyl exposed to the continued action of hydrochloric acid gas is resolved into biphosphomethyl and phosphotrimethylamine. The former is a yellow, non-volatile, inodorous, and tasteless body.

b. Phosphobimethyl. $C^4H^6P=Me^2P$.—Colourless, transparent liquid, insoluble in water, and having an extremely repulsive odour. Boils at 250°; takes fire spontaneously in the air; and when slowly oxidized, is converted into a crystallizable acid. With hydrochloric acid it forms a solid, permanent, crystallizable compound, which, by the further action of the gas, is converted into a liquid, acid, less permanent substance, and is ultimately resolved into biphosphomethyl and phosphotrimethylamine. The crystallized hydrochlorate dissolves without alteration in water at 0°; but the solution when heated is converted, by decomposition of water, into an acid, which is also formed by oxidation of phosphotrimethylamine.

c. Phosphomethylamine. $C^2H^5P=H^2,Me,P$.—Spontaneously inflammable gas, which unites with hydrochloric acid into a solid compound. By contact with water, this compound is instantly resolved into hydrochloric acid and gaseous phosphomethylamine. With an equal volume of oxygen this substance forms a very acid liquid.

d. Phosphotrimethylamine. $C^6H^9P=Me^3P$. — Mobile liquid, which boils at 40°, exhibits very strong basic properties, and is converted by oxidation into an acid.

The names and formulæ above given to the from Löwig's *Grundriss der org. Chemie*, S. 378. regards them as compounds of the three phosphid and PH^3 with 1, 2, and 3 At. methylene, C^2H^2, r yellow solid $a = P^2H^3,C^2H^2$; the inflammable liquid b compound $d = PH^3,3C^2H^2$. Similarly, the compoun PH^3,C^2H^2.

No detailed account of these compounds has y

¶ Zinc-methyl. C^2H^3Z

FRANKLAND. *Chem. Soc. Qu. J.* 2, 29.

Formed by the action of zinc on iodide of m methyl is heated with excess of granulated zinc i crystalline substance is formed, which, when distil hydrogen, yields zinc-methyl in the form of a co having a peculiarly penetrating and nauseous od fire spontaneously on coming in contact with air o a brilliant greenish blue flame, and forming dense of zinc. Its vapour, mixed with a large excess of burns with the characteristic blue flame, depositing within it, a black crust of metallic zinc surround This deposit is easily distinguished from arsen evolution of hydrogen in dilute hydrochloric acid, which gives no precipitate with sulphuretted hy zinc-methyl is highly poisonous, producing shortly symptoms of poisoning by zinc. It decompose potassium, the small tube containing a few drops red-hot under water; the products of the decompos zinc and 1 At. marsh-gas; thus:

$$C^2H^3Zn + HO = ZnO + C^2H^4$$

	Calculation, according to Frankla	
2 C	12·0	.....
3 H	3·0	.....
Zn	32·2	.....
C^2H^3Zn	47·2	.....

Zinc-methyl appears to be a radical capable o chlorine, &c. (Frankland.) ¶

B. Secondary Series.

a. Secondary Nucleus. C^2SH.

Tersulphide of Methyl. $C^2H^2S^3 = C^2HS,H^2S^2$?

Cahours (1846). *N. Ann. Chim. Phys.* 18, 260; abstr. *Compt. rend.* 22, 862.—[*Feleformaf.*]

A mixture of sulphomethylate of lime and pentasulphide of potassium yields by distillation, first, $C^2H^2S^2$, then, when the heat has risen to 200°, an amber-coloured distillate, which is but slightly altered by boiling, and exhibits with chlorine and nitric acid the same reactions as the compound $C^2H^2S^2$ (p. 283). (Cahours.)

			Cahours.
2 C	12	19·05	19·47
3 H	3	4·76	4·82
3 S	48	76·19	75·60
$C^2H^2S^3$	63	100·00	99·89

Sulphoform. $C^2HS^3 = C^2HS,S^2$?

Bouchardat (1837). *J. Pharm.* 23, 12; also *Ann. Pharm.* 22, 234.

A mixture of 1 pt. iodoform, C^2HI^3, and 3 pts. cinnabar, is gently heated in a small retort, and the fire removed as soon as the action begins. Iodide of mercury then distils over, accompanied by undecomposed iodoform, and a few drops of sulphoform (amounting to 1 per cent. of the iodoform used); it appears, however, still to contain iodine.—(Sulphoform is not obtained by boiling alcoholic potash with sulphur, or by heating iodoform with any of the higher sulphides of potassium.)

Orange-yellow oil, which sinks in oil of vitriol. Has a sulphurous and aromatic odour, and a very sweet and aromatic taste.

It is gradually decomposed by oil of vitriol. With aqueous alkalis it yields a metallic sulphide and an alkaline formiate. Dissolves very sparingly in water, to which it imparts its taste. Soluble in alcohol and ether. (Bouchardat.)

b. Secondary Nucleus. C^2IH.

Iodoform. C^2IH,I^2

Serullas. *Ann. Chim. Phys.* 20, 165; also *Schw.* 35, 493.—*Ann. Chim. Phys.* 22, 172; also *Schw.* 41, 416; also *N. Tr.* 9, 1, 98.—*Ann. Chim. Phys.* 25, 311; also *Schw.* 41, 436; also *Kastn. Arch.* 2, 1.—*Ann. Chim. Phys.* 29, 225; also *Schw.* 55, 328; also *Pogg.* 15, 70; also *Kastn. Arch.* 16, 147.—*Ann. Chim. Phys.* 39, 230.

Ferrari & Frisiani. *Brugn. Giorn.* 15, 241.

Taddei. *Brugn. Giorn.* 16, 65, and 167.

SCANLAN. *Ann. Phil.* 26, 14; also *Schw.* 45, 382.
MITSCHERLICH. *Pogg.* 11, 162, and 33, 334.
DUMAS. *Ann. Chim. Phys.* 56, 122; abstr. *Pogg.*
BOUCHARDAT. *J. Pharm.* 23, 1; also *Ann. P*
Pharm. 3, 18.
ST. EVRE. *Compt. rend.* 27, 533; abstr. *Jahresbe*

Kohlenhydriod, Formyliodid, Iodoforme, [*Scheformasch*].—Formerly: *Solid Iodide of Hydro fester Iodkohlenwasserstoff, Iodkohlenstoff, Periodu*

Discovered and examined by Serullas in 182 was established by Dumas in 1834.

Formation. 1. By the action of iodine and potash or soda on aqueous alcohol, aqueous ether ethyl (Bouchardat); also by the action of iodine a (Inglis.) Its formation from alcohol will be fully with its preparation (*vid. inf.*)—2. By the action of potash on dilute wood-spirit. (Lefort, *Compt. r* in this manner:

$$C^2H^4O^2 + 4I + KO = C^2HI^3 + KI$$

3. Also, though in small quantity, by the action, iodine and 1 pt. bicarbonate of potash dissolved i quantities of grape-sugar, common sugar, milk-su albumin, fibrin, casein, legumin, or gelatin. (Millo also *J. pr. Chem.* 37, 53.) Iodoform is not (Bouchardat), volatile oils or resins (Millon), or 4. When a stream of coal-gas is passed slowly anc over iodine, iodoform is produced, together with iodoform, together with Faraday's compound, C^4H^4 by alcohol, and precipitated by aqueous potash. (17, 1; also *J. pr. Chem.* 21, 115.)—5. Small qua sometimes obtained by passing iodine-vapour anc charcoal heated to redness in a glass or porcelain

Preparation. The production of iodoform f potash (or soda), requires 4 pts. iodine to 1 pt. attended with great evolution of heat, and there a the iodoform, iodide of potassium, acetate of ethyl, In some forms of the process, a small quantity of wise produced. When iodine and potash are adde to dilute alcohol, each successive portion of iodine the mixture brown, and each portion of potash s again, iodoform is produced without further acetate of ethyl, iodide of potassium, and traces of if the successive quantities of potash added are destroy the brown colour, so that the iodine alv acetate of ethyl is produced, but no iodoform, heated to 60°. (Bouchardat.)—Bouchardat suppo always produced in the first instance, and aft iodoform, as, according to his experiments, acetic form with potash and iodine than alcohol.—It is that two different decompositions of the alcohol

the one yielding iodoform and formiate of potash, the other producing acetic ether, which may then, by the further action of potash and iodine, be likewise converted into iodoform. The first of these decompositions takes place, as stated by Liebig (*Chim. org.*) in the manner represented by the equation:

$$C^4H^6O^2 + 8I + 6KO = C^2HI^3 + 5KI + C^2HKO^4 + 4HO.$$

According to this equation, 1,008 pts. (8 At.) iodine yield 391 pts. (1 At.) iodoform = 100 : 38·79.—Instead of this 38 per cent., however, the actual product is only 19 per cent., because part of the alcohol is converted, by the other mode of decomposition, into acetic ether, as follows:

$$2C^4H^6O^2 + 4I + 4KO = C^8H^8O^4 + 4KI + 4HO.$$

The quantity of iodoform obtained varies accordingly as the circumstances of the preparation favour the former or the latter mode of decomposition. The formation of iodoform appears to be especially favoured by heat, by a comparatively small quantity of alcohol, and an excess of potash. For in the first mode of decomposition, 1 At. alcohol is acted upon by 8 At. iodine and 6 At. potash; in the second, by only 4 At. iodine and 4 At. potash. When the potash is in excess, its predisposing affinity for formic acid favours the production of that compound. But if the potash and iodine are in too great excess, a large portion of the iodine is converted into iodide of potassium and iodate of potash, and thereby rendered unavailable for the preparation of iodoform. This loss may be avoided, as first pointed out by Mohr (*Ann. Pharm.* 19, 12), by using the potash (or soda) in the form of carbonate, inasmuch as aqueous alkaline carbonates do not yield iodates when treated with iodine. On this circumstance are founded the more recent methods of preparing iodoform. If the iodine be kept constantly in excess, a temperature of 60° is necessary, according to Bouchardat, to the formation of iodoform, even when an alkaline carbonate is used; according to Filhol, on the contrary, iodoform is produced either at an elevated temperature or in the cold, if the iodine is only in slight excess; but with a great excess of iodine, no iodoform is obtained, even on the application of heat. In any case, however, if the right proportion between the materials be preserved, the quantity of iodoform obtained is somewhat increased by elevation of temperature. Finally, since, under the most favourable circumstances, viz., when decomposition takes place wholly according to the first mode, only 3 atoms of iodine out of 8 are actually employed in the production of iodoform, the remaining 5 being converted into iodide of potassium, the product, as shown by Filhol, will be greatly increased, if these 5 At. iodine be again set free by passing chlorine through the liquid (*vid. inf.*)

Other theories of the production of iodoform have been given by Mitscherlich (*Pogg.* 11, 163), Poggendorff (*Pogg.* 37, 97), and Bouchardat (*J. Pharm.* 23, 3).

1. Iodine and potash or soda are made to act on aqueous alcohol, and the resulting iodoform is separated either by evaporating the alcohol or by precipitating with water.—*a.* A solution of potash in alcohol of 35° Bm. is added to a solution of iodine in alcohol of 35° Bm. till the liquid is decolorized; the filtrate is then diluted with a little water; the whole of the alcohol driven off by gentle heat; and the crystals which separate, washed on a filter and dried. (Serullas.)—*b.* To a solution of potash in alcohol of specific gravity 0·850, a small quantity of alcoholic potash-solution is added, leaving the iodine slightly in excess; the iodoform pre-

cipitated by diluting the liquid with a large
purified from admixed iodate of potash by treati
or by redissolving it in alcohol. (Taddei.)—*c.*
with 2 pts. hydrate of potash and a small qu
solution of 1 pt. iodine in 6 pts. alcohol of 36° I
portions; and the liquid filtered. On cooling—
only a small quantity of water has been used,
crystals are deposited, This mixture of iodine,
also be distilled, and the receiver changed as
over colourless; from this distillate, the iodoform
a state of great purity. (Ferrari & Frisiani.)—T
iodine, potash is added till the colour is destr
from the iodate of potash which settles at the bot
by distillation, and the remaining liquid left to c
form crystallizes out. (Scanlan.)—Iodine and aq
added alternately, in small quantities, and wi
dilute alcohol—each portion of iodine being suffi
and each portion of potash sufficient to decoloriz
has taken up 4 pts. of iodine. The mixture, whi
the operation, deposits, on cooling, the whole of
to 19·25 per cent. of the iodine used. (Boucha
10 hydrate of potash or soda, 25 alcohol, and 75
perature of the air, deposit crystals of iodate
however, immediately disappear, on the applica
tion of a trace of iodoform. If the iodine, al
heated to 60°, and then the hydrate of potash
scales are produced; the former then disappea
iodine, 8 or 10 pts. of pulverulent iodoform are o
colour. (Clary.)—*g.* When a mixture of 10 pt
75 water, is heated to 60°, and ammonia the
becomes decolorized, 6·8 pts. of iodoform are ob
of iodine. (Clary.)—*h.* Serullas, in his first exp
was necessary to use potassium or the antimonid
instead of potash; but these alkali-metals are
evolution of hydrogen, into alkalis, and act onl
introduced one of these metals, by small success
quantity as not to produce complete decoloration
tion of iodine in alcohol of 36° Bm.; precipitated
with water; and purified it by solution in alcoho

2. Hydrated alcohol is acted upon by iodin
bicarbonate of potash, soda, or ammonia.—*a.*
5 pts. carbonate of potash, 6 iodine, 6 alcol
5 : 6 : 3 : 18. The water is put into a long-ne
carbonate of potash, then the iodine, dissolved
alcohol is added, and the mixture heated till it
cooling, nearly all the iodoform (amounting to 1
used) crystallizes out, so that the mother-liquor
by water, and only yields a small quantity of
carbonate of potash, when evaporated to dryn
weak alcohol. (Alcoholic iodine does not act
potash; but, on the addition of water, iodoform
trated solutions of carbonate of potash in wate
agitated together in the cold, do not act upon
and form distinct layers when left at rest. Bu

the lower stratum disappears entirely, provided the quantity of iodine-tincture be sufficient, and the decolorized liquid deposits iodoform on cooling.) (Mohr, *Ann. Pharm.* 19, 12.)—*b.* 10 pts. iodine and 10 pts. bicarbonate of soda are added to a mixture of 100 pts. water and 13 pts. alcohol, and the mixture gently heated in the water-bath for 2 or 3 hours, till its colour disappears (during this time acetic ether is formed, and if the heat be too strong, iodine evaporates). More iodine is then added in small portions, till the brown colour which it produces, becomes permanent, after which the liquid is left to cool, and the crystals are collected on a filter. By this process, 100 pts. of iodine yield from 12 to 15 of iodoform.—By certain modifications of the process, 100 pts. of iodine may be made to yield different quantities of iodoform, as follows: 100 pts. iodine, 100 monocarbonate of soda, 250 alcohol, and 750 water, yield 11·3 pts. of iodoform.—100 pts. iodine, 100 bicarbonate of potash, 250 alcohol, 750 water: from 10 to 12 pts.—100 pts. iodine, 100 monocarbonate of potash, 250 alcohol, 750 water: 10·7 pts.—Similarly, with carbonate of ammonia, added after the other ingredients have been heated to 60°, the product amounts to 12·5 pts.; in this case, acetate of ammonia and a small quantity of iodine are given off, as well as acetic ether.—Similarly, with acetate of potash and a little ammonia: 15·2 pts.; in this case, acetic ether and acetate of ammonia are given off. (Clary, *N. J. Pharm.* 6, 51.) The liquids filtered from the iodoform in the first and second processes yield, on evaporation and ignition, iodide of potassium or sodium, mixed with alkaline carbonate.

3. The same processes as in 2, with the addition of subsequently passing a stream of chlorine through the liquid.—A solution of 2 pts. crystallized carbonate of soda in 10 pts. water is mixed with 1 pt. of alcohol; the mixture heated to 60° or 80°; and 1 pt. of iodine added by small portions, waiting each time till it dissolves, and the liquid again becomes colourless. Towards the end of the operation, iodoform separates out, and may be collected on a filter. The filtrate, still warm, is again heated to between 60° and 80°; 2 pts. of carbonate of soda again dissolved in it; and chlorine gas passed quickly through the liquid, which must be constantly agitated, in order that the separated iodine may be uniformly diffused through it. The iodine must be in excess during the whole process; a considerable quantity of iodoform is then produced. When this formation ceases, the stream of chlorine is interrupted, and after the liquid has become decolorized, the iodoform is collected on a filter. The filtrate, if again treated with chlorine, yields a little more iodoform. The product obtained from 100 pts. of iodine varies from 42 to 45 or 50 pts. (The rest of the iodine may be obtained from the filtrate by treating it, after evaporation, with excess of sulphuric or nitric acid, and purified by washing with cold water. If borax be substituted for the carbonate of soda, a product of equal amount will be obtained, but phosphate of soda yields a much smaller product). (Filhol, *N. J. Pharm.* 7, 267.)

Properties. Lemon-yellow, opaque, nacreous laminæ. (Serullas, Scanlan.) Lemon-yellow, truncated hexahedrons (rhombohedrons?). (Ferrari & Frisiani.) White, shining scales. (Taddei.) Sp. gr. about 2 000. (Serullas.) Friable, soft to the touch. (Serullas.) Volatilizes gradually when exposed to the air, quickly and without decomposition at 100°, (Serullas, Taddei), and may be distilled with water without decomposition. (Scanlan.) Has an aromatic odour, like that of saffron, (Serullas, Scanlan), and excites coughing. (Ferrari & Frisiani.) Its taste is scarcely

perceptible when alone; but the alcoholic solution has a sweet taste. (Serullas.) Tastes sweet, and leaves an unpleasant after-taste. (Taddei.) Tastes like nitrous ether, and acts upon the human body like iodine. (Ferrari & Frisiani.)

				Serullas.	Dumas.	Mitscherlich.
2 C	12	3·07	3·13	3·20		
1 H	1	0·26		0·33	0·22	
3 I	378	96·67	96·00	96·47		
C^2HI,I^2	391	100·00		100·00		

Decompositions. 1. Iodoform fuses between 115° and 120°, volatilizing partly undecomposed, and partly resolved into iodine-vapour and hydriodic acid gas, with a residue of shining charcoal. (Serullas.) According to Taddei, nothing but iodine-vapour is evolved in this decomposition.

2. Chlorine instantly decomposes iodoform. When no water is present and the chlorine is in excess, there are formed hydrochloric acid, chloride of iodine, and a white substance containing carbon, which may be freed from hydrochloric acid and chloride of iodine by washing with water: it is greasy to the touch, gives off, when moderately heated, a vapour smelling like camphor, and leaves a residue of charcoal; it is insoluble in water, but dissolves readily in alcohol, and still more readily in ether.—The same decomposition takes place on introducing iodoform into a vessel containing protochloride of iodine, which then becomes strongly supersaturated with iodine.—When the quantity of chlorine is smaller, and water is afterwards added, there is separated, instead of the white substance, a small quantity of an oily matter, heavier than water, greasy to the touch, and having a very powerful odour, like that of turpentine.—When chlorine acts upon iodoform in presence of a small quantity of water, the products are hydrochloric acid, chloride of iodine, and phosgene, even if the quantity of chlorine be small. (Serullas):

$$C^2HI^3 + 2HO + 8Cl = 2CClO + 3HCl + 3ICl.$$

3. Two parts of bromine instantly decompose 1 pt. of iodoform, with evolution of heat and a hissing noise, yielding bromide of hydrocarbon (bromiodoform; according to Bouchardat) and bromide of iodine. (Serullas.)—4. Aqueous hypochlorous acid acts violently on iodoform, giving off chlorine, carbonic acid, and carbonic oxide, forming aqueous hydrochloric acid and iodic acid, and separating iodine, which, if the hypochlorous acid is in excess, is converted into iodic acid. (Balard.)—5. A dry mixture of iodoform and pentachloride of phosphorus in a well-closed flask decomposes instantly on the application of heat; but if exposed to sunshine at ordinary temperatures, it remains unaltered for three months, and then decomposes in like manner, yielding a solid mixture of iodide of phosphorus and chloride of iodine, which is soluble in water, and a red liquid, insoluble in water, which is instantly decolorized by caustic potash, and behaves like a mixture of liquid iodide of carbon (chloriodoform, according to Bouchardat), with a very small quantity of Dutch liquid, $C^4H^4Cl^2$. (Serullas.)—Possibly thus:

$$C^2HI^3 + PCl^5 = C^2HICl^2 + PI + ICl^2.$$

[May not the oily liquid which Serullas regards as C^4H^4,Cl, be really chloroform, C^2HCl^3 ?].—Chloriodoform is also obtained on distilling iodoform with corrosive sublimate (Mitscherlich), chloride of lead, chloride of tin, or calomel. (Serullas.)—6. Iodoform, heated with 3 times its weight

of cinnabar, yields a yellow sublimate of iodide of mercury, mixed with undecomposed iodoform, and a small quantity of an orange-yellow distillate, consisting of sulphoform. (Bouchardat.)—7. When iodoform is heated with cyanide of silver, or cyanide of mercury, rapid decomposition takes place, extending itself spontaneously, and yielding a sublimate of iodide of cyanogen, which, when cyanide of mercury is used, soon becomes mixed with iodide of mercury. (Bouchardat.)

8. A mixture of iodoform with an equal weight of mercuric oxide, very gently heated in a retort, undergoes violent decomposition, accompanied with great evolution of heat, and therefore extending itself spontaneously; water passes over together with formic and carbonic acid, and a mixture of mercurous and mercuric iodide remains. (Bouchardat.) The equation,

$$2C^2HI^3 + 8HgO = C^2H^2O^4 + 2CO^2 + 4HgI + 2Hg^2I,$$

would explain this reaction, were it not that, as observed by Bouchardat, water is formed at the same time.—9. When iodoform is boiled with aqueous potash-solution, part of it evaporates undecomposed, and the rest is resolved into formiate of potash and iodide of potassium. (Dumas.)

$$C^2HI^3 + 4KO = C^2HKO^4 + 3KI.$$

10. When iodoform is heated with zinc, iron, copper, mercury, or silver (not with gold or platinum), a metallic iodide is obtained together with charcoal and hydrogen gas. (Serullas.)—When 1 gramme of iodoform is heated with potassium to the melting point of the latter, the mass becomes incandescent, and a violent explosion is produced, which shatters the containing vessel, probably from sudden evolution of hydrogen. (Dumas.)—Sulphurous, sulphuric, hydrochloric and nitric acid do not decompose iodoform; according to Ferrari & Frisiani, however, it is decomposed by oil of vitriol.

¶ 11. When cyanogen gas is passed into an alcoholic solution of iodoform, till it is no longer absorbed, the liquid becomes heated, and acquires a violet colour; if it be then left at rest, it will deposit golden-yellow, prismatic crystals, grouped like vine-leaves. This crystalline mass treated with cold dilute alcohol, yields two different substances possessing the metallic lustre, viz., a violet compound, $C^4HI^2N = C^2HI^2Cy$, and a greenish golden-yellow substance containing less iodine. (St. Evre.) ¶

Compounds. Iodoform is not perceptibly soluble in water, aqueous acids, or aqueous alkalis, but dissolves very readily in alcohol (whence it is partially precipitated by water); also in ether, and in oils both fixed and volatile (Serullas); also in chloroform. (Bouchardat.)

Bromiodoform. C^2HI,Br^2.

Serullas. *Ann. Chim. Phys.* 34, 97; also *Schw.* 49, 241; also *Pogg.* 9, 338.—*Ann. Chim. Phys.* 39, 225; also *Schw.* 55, 328; also *Pogg.* 15, 70.

Bouchardat. *J. Pharm.* 23, 10; also *Ann. Pharm.* 22, 233.

Bromiodoforme; formerly *Bromide of Hydrocarbon, Bromide of Carbon, Bromkohlenwasserstoff, Bromkohlenstoff, Hydrocarbure de Brome.* [*Mefor-*

masch.]—Discovered by Serullas in 1817; its true composition was first recognized by Bouchardat.

Produced by the action of bromine on iodoform (p. 335).

Preparation. 2 pts. of bromine are brought in contact with 1 pt. iodoform; water added after the action has taken place, to dissolve the bromide of iodine produced; the aqueous fluid decanted; the free bromine removed from the bromiodoform by caustic potash; the liquid placed in a separating funnel provided with a stopcock, and left there till the solution of iodate of potash has risen to the top. The bromiodoform is then suffered to run out, and freed from liquid iodide of hydrocarbon, which is still present in small quantity, by leaving it for some time under very dilute potash-ley,—by which, however, some portion of the bromiodoform is decomposed. (Serullas.) [The liquid iodide of hydrocarbon mentioned by Serullas is, as shown by Bouchardat, C^2HICl^2; this compound cannot be produced in the above process, unless the bromine contains chlorine.]—1 pt. of bromine is sufficient to act on 1 pt. of iodoform, for it is not necessary that the iodine which separates should be converted into bromide of iodine; indeed, it is better to separate the bromiodoform from the iodine by decantation or by aqueous potash-solution; it is true that the potash produces iodate of potash, but this may be easily removed by careful washing with water and decantation. The bromiodoform must then be freed from the remaining potash solution by agitation with oil of vitriol, and from the latter by mechanical separation and rectification. (Bouchardat.)

Properties. Colourless oil, solidifying at 0° to a brittle, camphor-like mass, which does not melt till heated above +6°; heavier than water. Very volatile; has a penetrating ethereal odour, and a persistent, very sweet, but somewhat fresh and pungent taste. (Serullas.)

	According to Bouchardat.		
2 C	12	....	4·02
H	1	....	0·33
I	126	....	42·14
2 Br	160	....	53·51
C^2HI,Br^2	299	....	100·00

Contains about 1 At. iodine to 2 At. bromine. (Bouchardat.)

Bromiodoform does not become coloured by exposure to the air.—When sprinkled on red-hot porcelain, it gives off white fumes.—Paper moistened with it does not take fire, but diffuses yellowish red vapours of bromine. When immersed in water, it decomposes slowly, assuming a yellowish red colour, and depositing white flocks. By aqueous potash it is gradually converted into bromide of potassium and a gas. (Soubeiran.) Large quantities of bromine do not decompose it further. (Bouchardat.)

Dissolves sparingly in water, to which it imparts its sweet taste. (Serullas.)

Chloriodoform. C^2HI,Cl^2.

SERULLAS. *Ann. Chim. Phys.* 25, 314; also *Schw.* 41, 436.—*Ann. Chim. Phys.* 39, 225.
MITSCHERLICH. *Pogg.* 11, 164.
BOUCHARDAT. *J. Pharm.* 23, 6; also *Ann. Pharm.* 22, 229.

Discovered by Serullas in 1824; its true composition recognized by Bouchardat.—*Chloroiodoforme* (*Keformasch*); formerly, *Liquid Iodide of Hydrocarbon, flüssiger Iodkohlenwasserstoff, Protohydriodure de carbone.*

Formation. By heating iodoform with pentachloride of phosphorus, or with various metallic chlorides (p. 335).

Preparation. 1. By distilling iodoform with an equal weight of pentachloride of phosphorus.—*a.* The materials, perfectly dry, are intimately mixed in a glass mortar, and the mixture heated in a flask provided with a gas-delivery tube passing under very cold water, till the iodoform melts. At first a few vapours of iodine make their appearance; then the new red substance distils over, collecting under the water, to which it soon imparts its colour.—Iodine, iodide of phosphorus, and chloride of iodine, remain in the flask; if the heat were too long continued, these products would likewise pass over, and by the heat which they would develop on coming in contact with the water, would cause part of the chloriodoform to volatilize.—The liquid is separated from the supernatant acid water by the separating funnel, shaken up with aqueous potash, the latter also removed by the funnel, and the chloriodoform washed with water. Lastly, to free it from Dutch liquid C^4H^4,Cl^2 [chloroform?], it is repeatedly agitated with 5 times its bulk of oil of vitriol, till it sinks to the bottom (so long as any of the lighter fluid C^4H^4Cl remains mixed with the chloriodoform, it separates very slowly from the oil of vitriol); it is then separated from the oil of vitriol by means of the separating funnel, again purified with aqueous potash, and finally with water.—If the oil of vitriol be added before the first purification with potash, decomposition takes place, because the substance, before purification by potash, contains a chlorine-compound, probably protochloride of iodine, which is acted upon by oil of vitriol. Hence also the chloriodoform, when kept without purification by potash, gives off, after a while, pungent vapours of hydrochloric acid, and then yields with potash a precipitate of iodine. (Serullas.)—*b.* The mixture is distilled in a retort, the dark red distillate decolorized by aqueous potash, agitated with oil of vitriol, on the top of which it collects, then separated from the oil of vitriol, and purified by redistillation. (Bouchardat.)

2. By distilling iodoform with an equal weight of protochloride of mercury. (Mitscherlich, Serullas, Bouchardat.)

$$C^2HI^3 + 2HgCl = C^2HICl^2 + 2HgI.$$

The mode of proceeding is the same as above.

Properties. Transparent, pale yellow liquid (becoming opaque and whitish after agitation with water, from admixture of the latter). Does not solidify even at the lowest temperatures; volatilizes without decomposition. (Serullas.) Sp. gr. about 1·96. (Bouchardat.) Has a peculiar penetrating, ethereal and pleasant odour (Serullas), resembling that of chloroform. (Bouchardat.) Its taste is strongly and persistently sweet, but cooling at the same time, like that of peppermint. (Serullas.)

				Bouchardat.
2 C	12·0	....	5·72	..... 6·00
H	1·0	....	0·48	..... 0·51
I	126·0	....	60·06	
2 Cl	70·8	....	33·74	
C^2HI,Cl^2	209·8	....	100·00	

According to Bouchardat, the compound contains 2 At. chlorine to 1 At. iodine.—On distilling iodoform with a double instead of an equal weight of corrosive sublimate, a distillate is formed containing only 1 At. iodine to 5 At. chlorine [perhaps=C^2HICl^2,C^2HCl^3], and likewise sinking in oil of vitriol. (Bouchardat.)

Decompositions. 1. Chloriodoform exposed to the air or immersed in water in close vessels quickly assumes a rose-colour, which continually increases in depth. (Serullas.) Does not burn in the flame of a candle; its vapour mixed with oxygen gas is not set on fire either by the flame of a candle or by the electric spark. (Serullas.)—2. When poured on red-hot coals or pieces of red-hot porcelain, it gives off vapour of iodine and the odour of iodoform. (Serullas.)—3. In contact with chlorine gas, it solidifies and forms terchloride of iodine. (Serullas.)—4. Heated with strong potash-ley, it decomposes more readily than chloroform, being resolved into formiate of potash, iodide of potassium, and chloride of potassium. (Bouchardat.)

$$C^2HICl^2 + 4KO = C^2HKO^4 + KI + 2KCl.$$

5. Its vapour passed over red-hot iron yields iodide of iron, hydrogen gas, and a large quantity of charcoal; 1 gramme yields 3 centilitres of hydrogen gas. (Serullas.)—It is not decomposed by chlorine-water or oil of vitriol. (Serullas.)

Combinations. Sparingly soluble in water, to which it imparts in a high degree its taste and odour. It is miscible with Dutch liquid. (Serullas.)

c. Secondary Nucleus. C^2BrH.

Bromoform. $C^2HBr^3=C^2HBr,Br^2$.

Löwig. *Ann. Pharm.* 3, 295.
Dumas. *Ann. Chim. Phys.* 56, 120; abstr. *Pogg.* 31, 654.

Formylbromid, Perbromure de formyle, Bromoforme [*Meformam*]; formerly, *Liquid Bromide of Carbon, flüssiger Bromkohlenstoff.*

Discovered by Löwig in 1832; its true constitution was first recognized by Dumas.

Formation. In the decomposition of bromal by aqueous fixed alkalis. (Löwig.)—2. In the decomposition of wood-spirit (Lefort), alcohol or acetone (Dumas), by bromine and aqueous fixed alkalis.—3. By treating an aqueous solution of citric or malic acid with bromine (Cahours, *Compt. rend.* 21, 814); also by the action of bromine on aqueous citrate of potash. (Cahours, *N. Ann. Chim. Phys.* 19, 484.)—4. Nearly all indifferent organic substances, when distilled with diluted bromine, yield a watery distillate containing in solution a small quantity of bromoform. (Löwig.)

Preparation. Bromal is distilled with excess of aqueous potash, the watery distillate decanted from the bromoform, and the latter completely dehydrated by oil of vitriol. (Löwig.)—2. Alcohol or acetone is distilled with excess of aqueous bromide of lime; the watery stratum of the dis-

tillate separated from the oil which sinks to the bottom; the latter shaken up with oil of vitriol; separated therefrom by a pipette; rectified; placed for a considerable time in contact with chloride of calcium, and frequently agitated, to remove water and alcohol; and finally separated from the chloride of calcium which floats upon it. (Dumas.)—3. To a solution of 1 pt. hydrate of potash or soda in 1 pt. of wood-spirit, which is kept as cold as possible, bromine is added from time to time, till the liquid begins to show colour; and the bromoform, which soon goes to the bottom in the form of an oily layer, is rectified over chloride of calcium, which retains the undecomposed wood-spirit. (Lefort, *Compt. rend.* 23, 229.)—¶ 4. When bromine is added in successive small portions to a concentrated solution of citrate of potash, it disappears, the liquid becoming heated and carbonic acid escaping. If the addition of the bromine be continued till the effervescence ceases and the liquid acquires a permanent red colour, and the excess of bromine be then carefully removed by means of dilute potash, an oily colourless liquid having an aromatic odour sinks to the bottom. This liquid is a mixture of three different compounds, the most volatile of which is bromoform. (Cahours.) ¶

Properties. Transparent and colourless oil, of sp. gr. 2·13; has a remarkably pleasant, aromatic odour, and a characteristic sweet taste. (Löwig.) Less volatile than chloroform. (Dumas.)—¶ According to Cahours, its sp. gr. is 2·90 at 12°; boiling point, 152°; vapour density. 8·63. ¶

					Dumas.		Löwig.
2 C	12	....	4·75	.....	5·41		
H	1	....	0·39	.....	0·47		
3 Br	240	....	94·86	.....	94·12	.....	93·24
C^2HBr^3	253	....	100·00	.....	100·00		

Decompositions. 1. Vapour of bromoform passed through a red-hot glass tube, remains partly undecomposed, and is partly resolved into charcoal and bromine vapour. (Löwig.)—2. Bromoform by itself cannot be set on fire; a glass rod wetted with it, and held in the flame of a spirit-lamp, renders the flame dark and smoky. (Löwig.)—3. When boiled with potash, it decomposes much more readily than chloroform, because it is less volatile; the products of the decomposition are bromide of potassium and formiate of potash (Dumas):

$$C^2HBr^3 + 4KO = 3KBr + C^2HKO^4.$$

4. The vapour passed over red-hot baryta or lime, yields a metallic bromide, an alkaline carbonate, and a small quantity of charcoal; passed over red-hot iron, it yields bromide of iron surrounded with charcoal, but no gas [?]. Potassium does not act on bromoform at ordinary temperatures; but when heated in the vapour, it burns with a bright light, and forms bromide of potassium mixed with charcoal. (Löwig.)

Combinations. Bromoform dissolves very sparingly in water, imparting to that liquid its taste and odour.—Dissolves but little phosphorus or sulphur, but a large quantity of iodine.—Soluble in alcohol, ether, and volatile oils. (Löwig.)

d. Secondary Nucleus. C^2Br^2.

Protobromide of Carbon. C^2Br^2.

Löwig. *Das Brom und seine chemischen Verhältnisse.* Heidelberg (1829–42).—*Ann. Pharm.* 3, 292.

Solid Bromide of Carbon, fester Bromkohlenstoff [*Formem*].

Preparation. Bromide is added in successive portions to alcohol of 36° Bm., till the liquid, which becomes heated, begins to effervesce. The liquid is then left to cool; alcoholic potash added till the colour disappears; then water is added, and the alcohol left to evaporate at a gentle heat. On cooling, a lemon-yellow oil first separates out, then solid bromide of carbon; which may be purified by solution in alcohol and precipitation by water.—2. Absolute alcohol is distilled with bromine, and the lower reddish yellow layer, consisting of hydrobromic ether, C^4H^5Br, containing free bromine, is agitated with potash, whereupon the decolorized liquid becomes turbid in a few days, and deposits bromide of carbon.—3. When a mixture of ether and bromine which has been left to itself for a long time is distilled, hydrobromic acid passes over first, and afterwards liquid bromide of carbon [probably $C^4H^4Br^2$]. On mixing the brownish residue, first with potash and then with water, solid bromide of carbon is immediately separated in very large quantity, and may be collected on a filter. Völckel, (*Ann. Pharm.* 41, 119) on repeating this process with various proportions of ether and bromine, which were left to act upon each other for months, and adding potash to the residue of the distillation, obtained an oil which separated from the liquid, but nothing solid.—4. When bromine obtained from the Kreuznach salt-spring is saturated with aqueous potash, and the mixture evaporated, solid bromide of carbon often separates from it in the fused state, having been previously mixed with the bromine.

Properties. White, opaque, camphoroidal scales, greasy to the touch, very friable, heavier than water. The compound melts at 50°, forming a transparent and colourless oil; at 100° it volatilizes and sublimes in needles having a pearly lustre. Has a very aromatic odour, like that of nitrous ether; its taste is aromatic and burning at first, but afterwards cooling and persistently sweet.

				Löwig.
2 C	12	6·98		
2 Br	160	93·02		93·92
C^2Br^2	172	100·00		

Decompositions. The compound burns in the flame of a spirit-lamp, emitting fumes of hydrobromic acid, but goes out when removed from the flame. In the fused state, it is instantly acted upon by chlorine, yielding chloride of bromine [and a chloride of carbon ?].—When heated with mercury, or passed in the state of vapour over red-hot zinc-oxide, ferric oxide, or cupric oxide, it yields a metallic bromide and carbonic acid gas. Its vapour, passed over red-hot zinc, iron, or copper, is resolved into a metallic bromide and charcoal, without evolution of gas.

—Nitric, sulphuric, and hydrochloric acids exert no action upon it. The alcoholic solution does not render a silver-solution turbid, neither is it decomposed by boiling with potash.

Combinations. Solid bromide of carbon is slightly soluble in water, to which it imparts its sweet aromatic taste.—Dissolves readily in alcohol and ether. (Löwig.)

This compound is perhaps C^4Br^4.

e. Secondary Nucleus, C^2ClH.

Chloromethylase. C^2ClH.

Chlormethylas [*Formak*].—Discovered by Laurent in 1836 (*Ann. Chim. Phys.* 63, 382; also *J. pr. Chem.* 11, 236.)

Deposited in the form of an oil when chloracetate of methyl ($C^6H^3Cl^3O^4 = C^2H^3O, C^4Cl^3O^3$) is decomposed by potash. It is heavier than water; may be distilled without decomposition; is not decomposed by potash-ley; is insoluble in water, but dissolves in alcohol and ether.

				Laurent.
2 C	12·0	24·80		25·9
H	1·0	2·06		2·9
Cl	35·4	73·14		71·2
C^2HCl	48·4	100·00		100·0

Regarded by Berzelius (*Ann. Chim Phys.* 67, 312), as *chloride of formyl*, C^2H,Cl.

Chloroform. C^2ClH,Cl^3.

Soubeiran. *Ann. Chim. Phys.* 48, 131; also *J. Pharm.* 18, 1; abstr. *Schw.* 65, 104.—Further: *Compt. rend.* 25, 799; Soubeiran & Mialhé. *Ann. Pharm.* 71, 225; *N. J. Pharm.* 16; 5; *J. pr. Chem.* 48, 86; *Pharm. Centralb.* 48, 86; abstr. *Jahresber.* 1849, 711.

Liebig. *Ann. Pharm.* 1, 198; also *Pogg.* 24, 259.

Dumas. *Ann. Chim. Phys.* 56, 115; abstr. *Pogg.* 31, 653.

Regnault. *Ann. Chim. Phys.* 71, 577; also *Ann. Pharm.* 33, 328; also *J. pr. Chem.* 19, 210.

Various modes of preparation: *Ann. Pharm.* 19, 210.

Purification and properties: Gregory. *Proceedings of the Royal Society of Edinburgh*, 1850, 39; *Pharm. J. Trans.* 19, 580; *Chem. Gaz.* 1850, 189; *Jahresber.* 1850, 454.

Perchloride of Formyl, Formylchlorid, Perchlorure de formyle, Ether hydrochlorique de methylène bichloruré, Formène trichloré [*Keformak*].

Discovered by Soubeiran in 1831, as *Ether bichlorique;* by Liebig, in 1832, as *Chloride of carbon;* its true constitution was discovered by Dumas in 1834.—¶ Hutmann (*J. Chim. méd.* [3], 4, 476) states, on the authority of Porta's *Magia naturalis* (1567), and Scott's *Letters*

upon Demonology and Witchcraft, that it was known in former times, and used as a means of producing insensibility. ¶

Formation. 1. In the decomposition of C^2H^3Cl or $C^2H^2Cl^2$ by chlorine in sunshine. (Regnault.)—2. In the decomposition of chloral by aqueous fixed alkalis. (Liebig.)—3. In the decomposition of wood-spirit (Dumas and Péligot), of alcohol (Soubeiran), or of acetone, which yields a larger quantity of chloroform (Liebig), by aqueous chloride of lime containing excess of lime. Also by passing chlorine gas into alcoholic solution of potash. (Soubeiran.)—4. On mixing heavy hydrochloric ether first with alcoholic solution of potash, then with a large quantity of water. (Liebig.)—5. By boiling chloracetic acid with aqueous ammonia or potash. (Dumas.)—6. By heating acetate of potash with chloride of lime (Bonnet); ¶ or acetate of soda with chloride of lime (Böttger, *Polytechn. Notizblatt*, 1848, Nr. 1); or acetate of soda with hypochlorite of soda (Reich, *Arch. Pharm.* [27,] 55, 65).—7. By heating a mixture of alcohol and chloride of ethyl with chloride of lime (Pierloz-Feldmann, *J. Chim. méd.* [3], 4, 309.)—8. The oils of turpentine, lemons, bergamot, copaiba, and peppermint, heated with chloride of lime and water, likewise yield chloroform. (Chautard.) ¶

Preparation. 1. By mixing chlorine gas with gaseous chloride of methyl in a vessel exposed to the sun's rays (p. 287); the mixture of C^2HCl^3 and $C^2H^2Cl^2$ condensed in the two Woulfe's bottles is almost wholly converted into chloroform, by passing chlorine gas over it for some time without cooling the vessels. The remainder of the $C^2H^2Cl^2$ which passes over at first, may be separated by rectification with a fresh receiver. (Regnault.)—2. By distilling chloral with excess of aqueous potash, soda, or baryta, or with milk of lime; agitating the oily distillate repeatedly with water, separating it from the water as completely as possible by decantation, and distilling it with six or eight times its volume of oil of vitriol in a perfectly dry apparatus. (Liebig.)—3. Sixteen parts of chloride of lime are mixed with water, the decanted solution distilled with 1 pt. of wood-spirit, and the oil separated from the supernatant watery distillate, agitated with oil of vitriol, and rectified over finely pounded baryta. (Dumas & Péligot, *Ann. Chim. Phys.* 58, 15.)—4. The clear decanted solution of 6 pts. chloride of lime in 30 pts. of water, is gently heated in a retort with 1 pt. alcohol of 33° Bm.; the fire removed as soon as the mixture begins to boil up, the distillation then going on by itself till all the chloroform has passed over; the distillate (which consists of a lower stratum of chloroform, and an upper stratum of the same compound dissolved in dilute alcohol), purified from free chlorine by agitation with mercury, and then rectified in the water-bath; the upper layer removed; the lower layer introduced into a retort containing chloride of calcium, left there for several hours, and then distilled at a temperature not exceeding 70°. (Soubeiran.)—Dumas agitates the chloroform obtained by 3 and 4, after it has been separated from the watery layer, violently with oil of vitriol; separates it from the latter by means of a pipette; distils it in the water-bath with a small quantity of fresh oil of vitriol; then rectifies it over chloride of calcium, and treats it once more with oil of vitriol. Pure chloroform should not colour oil of vitriol.—5. Hydrate of lime is diffused through 24 parts of water, and chlorine passed through the mixture till the greater part of the lime has disappeared; milk of lime is then added in sufficient quan-

tity to produce an alkaline reaction; the liquid clarified by subsidence and decantation; 24 parts of it mixed with 1 pt. of wood-spirit, alcohol, or acetone; and the mixture, after 24 hours, distilled from a retort two-thirds filled with it. The distillate mixed with water deposits the chloroform, which may then be rectified in the water-bath, digested with chloride of calcium, and lastly distilled once more with oil of vitriol. (Liebig, *Chim. org.* 1, 576.)—6. A mixture of equal parts of acetate of lime and chloride of lime is distilled in an earthen retort, the chloroform precipitated from the distillate by water, and rectified over chloride of calcium. (Bonnet, *L'Institut*, 1837, Nr. 196, 47; also *J. pr. Chem.* 10, 207.—Possibly thus:

$$C^4H^3CaO^4 + 3(CaO,ClO) = C^2HCl^3 + 2CO^2 + 4CaO + 2HO.$$

¶ 7. By distilling 1 pt. oil of turpentine, with 8 pts. chloride of lime and 24 water. The mixture must be rapidly heated to set up the action, whereupon great frothing takes place and carbonic acid is evolved; after this, the chloroform distils over spontaneously; the residue contains formic acid. The oils of lemons, bergamot, copaiba, and peppermint likewise yield chloroform when thus treated. (Chautard, *N. J. Pharm.* 21, 88; abstr. *Compt. rend.* 33, 671; *Instit.* 1851, 402; *J. pr. Chem.* 55, 117, *Jahresber.* 1851, 501.) According to Soubeiran (*N. J. Pharm.* 21, 94), oil of turpentine treated in this manner yields but little chloroform. The action is difficult to regulate; and the resulting chloroform, even if rectified below 62°, emits an odour of turpentine when evaporated.

The preparation of chloroform has lately become an object of great commercial importance, on account of its extensive use as an anæsthetic agent. The following are the principal methods which have been given for preparing it economically from alcohol and chloride of lime:

a. 10 kilogrammes of commercial chloride of lime of 90° are diffused through 60 kil. water, and the mixture introduced into a copper still which it fills to about two-thirds. 2 kil. alcohol of 85 p. c. (=38° Bm.) are then added, the mixture quickly heated, and the distillation conducted just as in 4. The resulting chloroform is separated by decantation from the watery liquid, shaken up with water, then with carbonate of soda, afterwards dehydrated by chloride of lime, and distilled. (Soubeiran, *Compt. rend.* 25, 799.) This process has the disadvantage of requiring the use of dilute solutions of chloride of lime, in order to avoid the formation of other products, so that large stills have to be used for the preparation of comparatively small quantities; nevertheless, the whole operation does not occupy much time, and may be repeated several times in the course of a day. The product appears to be greater, the more quickly the liquid is heated before the commencement of the operation; hence it is best to mix the chloride of lime at once with hot water in the still.—*b.* 10 lbs of chloride of lime are stirred up with 30 lbs. of water in a copper still, and 1 lb. of alcohol of 80 p. c. added. The mixture is left to stand over night, stirred up again in the morning, and repeatedly distilled over a wood fire. The heavy chloroform, after separation from the watery stratum of the distillate, is agitated with milk of lime in sufficient quantity to remove the free chlorine, and then rectified in a glass retort in the vapour-apparatus, or over a spirit-lamp. If good chloride of lime has been used, the chloroform obtained amounts to 5 or 6 ounces. The product is diminished by using alcohol either stronger

or weaker than 80 p. c. In four distillations made with the above proportions, but with different chloride of lime, the products varied from 3 oz. 5 drm. 2 scr. to 5 oz. 3 drm. 1½ scr. (Meurer, *Arch. Pharm.* [2], *53*, 282; *Pharm. Centr.* 1848, 154.)—*c.* 5 kilogrammes of burnt lime, previously slaked, and 10 kil. of commercial chloride of lime, are mixed with 35-40 litres of water; from 1 to 1½ litre of 85 per cent. alcohol added; and the mixture heated as quickly as possible to the boiling point. As soon as the neck of the still becomes hot, the fire is removed, and the distillation left to go on by itself. The liquid which floats upon the chloroform is removed, and used in the following distillation. 4½ litres of alcohol, in four successive operations, yield 2620 grm. of rectified chloroform. The chloroform thus obtained is at once free from chlorine, and consequently the distilling vessels are not so much attacked as in Soubeiran's process. (Larocque & Hurault, *N. J. Pharm.* 13, 97; *J. Chim. méd.* [3], 4, 150; *Compt. rend.* 26, 103; *Instit.* 1848, 38; *J. pr. Chem.* 43, 296; *Pharm. Centr.* 1848, 202.)—*d.* 30 litres of water and 5 kilogrammes of good chloride of lime, are introduced into a stone jar standing in a copper-boiler, which serves as a water-bath, the mixture well stirred, and a kilogramme of 86 per cent. alcohol immediately poured in. To the mouth of the jar is adapted a glass tube, bent downwards, and passing into the tubulus of a glass globe. Into the latter there likewise passes a glass tube, bent twice at right angles, its free extremity being inserted into a test-tube surrounded with ice. When the whole is properly luted, the water in the copper vessel is made to boil, and the boiling continued as long as any oily drops condense in the tube. The use of the water-bath presents this advantage, that the chloroform passes over unaccompanied by aqueous vapours. A well-conducted operation yields 250 grammes of chloroform, which are purified in the ordinary way. (Godefien, *N. J. Pharm.* 13, 101; *Pharm. Centr.* 1848, 202.)—*e.* 10 pounds (10 *civilpfund*) of chloride of lime are mixed in a still with 18 measures (18 *maass*) of water; 40 ounces of 84 per cent. alcohol added; the still-head immediately put on, and carefully luted; and the receiver attached perfectly airtight. After 12 to 16 hours, by which time the luting becomes perfectly dry, a very gentle heat is applied by means of a charcoal fire, so as to produce a temperature not quite amounting to 60° R. (75° C.) After three or four hours, the chloroform begins to distil, and the distillation is completed in half an hour. According to the mean of 17 experiments, the product amounts to 9½ ounces. (F. Carl, *Pharm. Centr.* 1848, 236.)—*f.* A mixture of 250 grammes (8 oz.) of chloride of ethyl, 125 grammes (4 oz.) of alcohol of 39°, 2 kilogrammes (4 lb.) of dry chloride of lime, and 4 kilogrammes (8 lb.) of water is distilled, and the chloroform separated in the usual way from the other products in the distillate. The product is 90 grammes (2½ oz.) of chloroform, at an expense of 2 frc. 15 cent. The liquid separated from the chloroform is used in subsequent preparations, only half the quantity of alcohol and chloride of ethyl being then added. (Pierloz-Feldmann, *J. Chim. méd.* [3], 4, 309; *Instit.* 1848, 196; *Pharm. Centr.* 1848, 830; *Arch. Pharm.* [2], 56, 185; *J. pr. Chem.* 44, 244.)

g. Preparation on the large scale. (Kessler, *N. J. Pharm.* 13, 162; *Pharm. Centr.* 1848, 236.) The apparatus used consists of a large leaden cylinder, the sides of which are soldered with lead. Through the middle of the upper end passes a vertical rod, provided at the bottom with fans, and at the top with a curved handle, its lower extremity turning on a pivot in the base of the cylinder. By means of this arrangement, the

mixture may be stirred up during the operation, and the heat thereby equally diffused. In the upper end of the cylinder there is also a wider aperture, which can be closed at pleasure, and through which the materials are introduced; through a third aperture is inserted the delivery-tube, by which the chloroform vapour is conveyed to the condensing apparatus. Opposite to this tube there passes through the upper base of the cylinder, a leaden tube, widened above like a funnel, and reaching just below the surface of the liquid. Into this funnel-tube, at some distance below the funnel, is inserted a steam-pipe, serving to convey steam from a boiler to the inside of the funnel-tube; and above the point of insertion of the steam-pipe, the funnel-tube is furnished with a cock, which, when open, allows the steam to pass upwards to the funnel-tube, and, when shut, directs it into the mixture in the cylinder. This cock serves to regulate the supply of vapour, and thereby regulates the heat. The chloroform vapour passes upwards through a worm-tube, enclosed in a condensing vessel, to a cooled Woulfe's apparatus, the last bottle but one of which is half filled with alcohol, and the last with cotton saturated with alcohol. A close-shutting wooden cask may be used instead of the leaden cylinder. 40 kilogrammes of the strongest chloride of lime are introduced into the cylinder, by means of a four-cornered wooden funnel adapted to its widest aperture, and provided, near its lower extremity, with two horizontal rollers pressing against each other, as in a rolling-mill; these, when turned by their handles, serve to drive the chloride of lime quickly into the cylinder. 4 kilogrammes of slaked lime are next introduced in the same manner, and then a hectolitre of water, at a temperature of 80° to 90°, is poured in. The apparatus is now thoroughly luted, and the contents well mixed by turning the fans. 4 kilogrammes of commercial alcohol are then poured in, together with the residues of former operations. If the distillation of the chloroform does not immediately begin, steam is admitted from the boiler, and stopped as soon as the distillation is fairly set up. If the evolution of vapour becomes too rapid, cold water is poured in through the funnel-tube. When the reaction is complete, steam is again admitted into the cylinder, and the contents, which are now heated to 100°, frequently stirred. After 3 litres are distilled off, the residue contains scarcely any chloroform or alcohol. The contents of the cylinder are discharged by an opening in the bottom, the liquid portion drawn off, and used in the next operation. The alcohol in the last two Woulfe's bottles likewise serves for the following preparations, and the process may be repeated three or four times in a day. 1 kilogramme of chloride of lime yields from 60 to 80 grammes of pure chloroform.

According to Siemerling (*Arch. Pharm.* [2], 53, 23), the largest quantity of chloroform, in proportion to the alcohol used, is obtained from a mixture of 8 pts. chloride of lime, 1 pt. quicklime, 1 pt. alcohol, and 40 pts. water; the rectified chloroform thus produced, amounts to nearly one-third of the alcohol consumed (8 grm. chloroform from 25 grm. alcohol). The use of acetone for the preparation of chloroform is not advantageous, because the price of it is high, and the product does not exceed $\frac{1}{3}$ of the acetone used. This proportion was obtained by first distilling 30 grm. acetone with 150 grm. chloride of lime mixed with water, and rectifying the watery distillate with 40 grm. chloride of lime. Chloroform obtained from wood-spirit has an empyreumatic odour, and

always blackens when agitated with oil of vitriol. The largest product was 6 grm. chloroform from 50 grm. wood-spirit.

Impurities. Chloroform may be contaminated with alcohol, ether, and empyreumatic oils. According to Soubeiran, pure chloroform sinks in a mixture of equal parts of oil of vitriol and water. According to Kessler, chloroform containing alcohol diminishes in volume on the application of this test. The presence of alcohol causes opalescence when the chloroform is mixed with water, whereas pure chloroform remains clear. (Mialhé, *J. Chim. méd.* [3], 4, 279.)—Chloroform containing alcohol acquires a green colour when mixed with chromic acid or with sulphuric acid and bichromate of potash; pure chloroform produces no green colour. (Cottell, *J. Chim. méd.* [3], 4, 257, 491; *J. Pharm.* [3], 13, 359; *J. pr. Chem.* 44, 246.)—Chloroform prepared from wood-spirit is much less pure than that obtained from alcohol. The former is specifically lighter than the latter, has a repulsive empyreumatic odour, and produces unpleasant sensations when inhaled. It is contaminated with an empyreumatic oil containing chlorine, and burning with a smoky flame; the proportion of this impurity is 3 pts. in 50. This oil is lighter than water, begins to boil at 85°, but the boiling point afterwards rises to 133°. It cannot be completely separated by simple rectification. By distillation with sulphuric acid, it is nearly, but not quite, destroyed. A similar oil, but in smaller quantity, is likewise obtained in the preparation of chloroform from alcohol; 20 kilogrammes of chloroform from alcohol, yielded, when rectified over the water-bath, only 40 gram. of residue consisting of this oil. It is heavier than water, has an odour different from that of the oil obtained from wood-spirit, and its boiling point varies from 68° to 117°. (Soubeiran & Mialhé.) According to Gregory, impure chloroform may be recognized by the disagreeable odour which it leaves after evaporation, on a cloth which has been moistened with it, and by the yellow or brown colour which it imparts to pure oil of vitriol when agitated therewith. Pure chloroform placed upon oil of vitriol produces a contact-surface convex downwards; impure chloroform gives a plane contact-surface. To purify chloroform, Gregory agitates it and leaves it in contact with oil of vitriol till the latter is no longer coloured by it, then removes the chloroform, and places it in contact with a small quantity of peroxide of manganese, to free it from sulphurous acid. According to Abraham (*Pharm. J. Trans.* 10, 24), chloroform thus purified quickly decomposes, and is afterwards found to contain hydrochloric acid and free chlorine. According to Christison (*Pharm. J. Trans.* 10, 253; *Chem. Gaz.* 1850, 371), chloroform keeps well after being once treated with oil of vitriol; but the continued action of that liquid (especially if contaminated with nitrous acid,) exerts a decomposing action upon it. ¶

Properties. Transparent and colourless oil, of specific gravity 1·480 at 18° (Liebig); 1·491 at 17° (Regnault); ¶ 1·493....1·497 (Swan, *Phil. Mag. J.* 33, 38); 1·496 at 12°; that of the impure chloroform obtained from wood-spirit is only 1·413 (Soubeiran and Mialhé); 1·500 at 15·5° (Gregory); 1·52523 at 0°. (Pierre.) ¶—In contact with platinum wire, and with the barometer at 27″ 7‴, it boils in a dry vessel at 60·8°, but in presence of water, at 57·3° (Liebig); boils at 61° (Regnault); at 70° (Soubeiran); at 63·5°, the barometer being at 772·52 mm. (Pierre.)—Vapour-density = 4·199 (Dumas); 4·230. (Regnault.) ¶ Chloroform

remains liquid and transparent at −16° (Pierre), but may be solidified by the cold produced by its own evaporation; when it is thrown upon a double filter, the rapid evaporation at the edges causes the remaining portion to solidify in white tufts. (Soubeiran & Mialhé.) ¶—It has a very pleasant, penetrating odour, a sweet, fiery taste, and its vapour, when inhaled, produces a sweet taste in the palate.—¶ The inhalation of a small quantity of the vapour causes excitement, similar to that produced by nitrous oxide; but a larger quantity produces insensibility to pain, in fact, a kind of coma; hence it is extensively used in surgical operations.* According to Robin (*Compt. rend.* 30, 52), and Augendre (*Compt. rend.* 31, 679; *Instit.* 1850, 362), chloroform preserves meat from putrefaction (200 times its weight, according to Augendre). ¶

			Dumas.	Regnault.	Liebig.	Soubeiran.
2 C	12·0	10·07	10·21	10·16	11·68	13·76
H	1·0	0·84	0·92	0·92		2·20
3 Cl	106·2	89·09	88·87		88·18	82·98
C^2HCl^3	119·2	100·00	100·00			98·94

	Vol.	Density.
C-vapour	2	0·8320
H-gas	1	0·0693
Cl-gas	3	7·3629
Chloroform-vapour	2	8·2642
	1	4·1321

Decompositions. ¶ 1. Chloroform decomposes when exposed to air and light, with formation of chlorine, hydrochloric acid and other products; but when kept under water, it remains unaltered. (Marson, *Pharm. J. Trans.* 8, 69; *Pharm. Centr.* 1848, 831.) ¶ 2. At a red heat, its vapour appears to be resolved, partly into sesquichloride of carbon and hydrogen gas, partly into carbon, hydrochloric acid and chlorine:

$$2C^2HCl^3 = C^4Cl^6 + 2H; \text{ and } C^2HCl^3 = C^2 + HCl + Cl^2.$$

2 grammes of chloroform, passed through a red-hot tube, deposit charcoal, and yield long, feathery crystals, having the odour of sesquichloride of carbon, C^4Cl^6, together with 7 cubic centimetres of gas, of which four are absorbed by water, and the other three burn with a green flame. (Liebig.) Chloroform thus treated, yields charcoal, together with fine needles of Julin's chloride of carbon, C^4Cl^2, and a mixture of chlorine gas with hydrochloric acid. (Regnault.) The vapour passed through a

* "For the introduction of this valuable remedy we are indebted to Dr. Simpson; and although ether, benzole, and many other liquids, can produce insensibility to pain, chloroform is of all the most powerful as well as the most manageable. Of course great care must be taken to insure its purity, for the oils which accompany it are very deleterious; and in administering it, one person should do nothing but watch the pulse and respiration of the patient and remove the chloroform if necessary. With due precaution, chloroform is very safe; and this precaution will prevent its being used in cases where its use is contra-indicated by the disease of the heart, or by marked tendency to apoplexy. In proof of its safety, it may be mentioned that in Edinburgh, where it must now have been used in upwards of 100,000 cases, no instance of a fatal result has occurred. Deaths have occurred elsewhere; but it is probable either that the chloroform was not pure, or that it was used in cases unfit for it, or, finally, that due care was not taken to prevent an overdose. That all these things can be avoided is proved by the results of the Edinburgh practice." (Gregory, *Handbook of Organic Chemistry*, 3rd Ed., Lond. 1852, p. 178.)

red-hot tube filled with coarsely pounded porcelain, deposits a large quantity of charcoal, and yields hydrochloric acid gas, mixed with small quantities of chlorine and a combustible gas; if the porcelain-powder be very coarse, the gas contains a large quantity of free chlorine, and in the cold part of the tube there is deposited a liquid which makes paper transparent, like an oil. (Soubeiran.)—3. Chloroform cannot be set on fire in the air, not even with the aid of a wick; but its vapour passed into the flame of a spirit-lamp, burns with smoke; and a mixture of chloroform and alcohol in equal measures, burns with a very smoky flame and pungent odour, producing hydrochloric acid. (Soubeiran, Liebig.) It imparts a green colour to the flame of a candle. (Liebig.)—4. Chloroform repeatedly distilled in a stream of dry chlorine, is resolved into HCl and C^2Cl^4. (Regnault.) When exposed to the sun in a bottle filled with dry chlorine, chloroform yields hydrochloric acid and a crystalline substance, probably a chloride of carbon, which, however, disappears when an attempt is made to collect it, being decomposed by the moisture of the air. (Laurent, *Ann. Chim. Phys*, 60, 318.)—5. Chloroform heated with nitric acid evolves but a small quantity of nitrous fumes. (Soubeiran.)—6. When kept under oil of vitriol, it gradually gives off vapours of hydrochloric acid. (Dumas, *comp.* p. 347.) The alcoholic solution of chloroform, mixed with nitrate of silver, does not deposit any chloride of silver, even in the course of a month. (Soubeiran.)—7. Boiled with potash-ley in a closed tube, it is resolved into formiate of potash and chloride of potassium; but the decomposition is imperfect (Dumas):

$$C^2HCl^3 + 4KO = C^2HKO^4 + 3KCl.$$

Chloroform is not decomposed by boiling with aqueous alkalis in an open vessel. (Liebig.) An alcoholic solution of potash decomposes it slowly at ordinary temperatures, but quickly on the application of heat, forming chloride of potassium and a yellow volatile oil, which separates on the addition of water, and smells like Roman cumin-oil. (Soubeiran.) Alcoholic potash boiled for a long time with chloroform produces formiate of potash. (Regnault.)—8. Chloroform vapour passed over ignited baryta or lime, yields metallic chloride, carbonate, and charcoal; if the heat be moderate, these products are not accompanied by any gas; but at a full red heat, carbonic oxide is produced by the action of the charcoal on the alkaline carbonate. (Liebig.) Heated baryta or lime becomes incandescent when chloroform vapour is passed over it, and is converted into metallic chloride, with deposition of charcoal and evolution of aqueous vapour and a combustible gas. (Soubeiran.)—9. Chloroform may be distilled over potassium without decomposition; but potassium heated in its vapour takes fire with explosion, forming chloride of potassium mixed with charcoal. (Liebig.) Chloroform is not decomposed by heating with cyanide of potassium, mercury, or silver, not even on the addition of alchohol. (Bouchardat.)

Combinations. Chloroform dissolves sparingly in water, to which it imparts its sweet taste. (Soubeiran.)

It dissolves phosphorus, sulphur, and iodine (Liebig); the iodine may be removed by potash. (Bouchardat.) It is insoluble in oil of vitriol.

It dissolves iodoform, depositing the greater part of it again on evaporation. (Bouchardat.)

Mixes in all proportions with alcohol (Soubeiran); whence it may be

partially precipitated by water (Liebig); a small quantity of chloroform forms, with weak alcohol, a very sweet, aromatic liquid. (Soubeiran.)

Dissolves readily in common ether. (Liebig.)

Bichlorinated Methyl-ether. C^2ClH,ClO.

Regnault (1839). *Ann. Chim. Phys.* 71, 396; also *Ann. Pharm.* 34, 29; also *J. pr. Chem.* 19, 271.

Formyl-Aci-Bichlorid (Berz.); *Bichlorformäther, Ether methylique bichloruré* [*Nakaformak*].

Obtained by the continued action of chlorine in bright daylight on mono-chlorinated methyl-ether. In sunshine the action is so violent that the mixture takes fire; in this case, also, C^2Cl^3O is produced.

Liquid; sp. gr. 1·606 at 20°; boils at about 130°. Vapour-density 6·367; smells like C^2H^2ClO, but fainter.—By the action of a larger quantity of chlorine in sunshine, it is converted into C^2Cl^3O. (Regnault.)

2 C	12·0	....	13·07	....	13·07	C-vapour....	2	.... 0·8320
H	1·0	....	1·09	....	1·12	H-gas	1	.... 0·0693
2 Cl	70·8	....	77·12	....	76·92	Cl-gas	2	.... 4·9086
O	8·0	....	8·72	....	8·98	O-gas	½	.... 0·5546
C^2Cl^2,HO	91·8	....	100·00	....	100·00		1	.... 6·3645

Copulated Compounds.

Sulphite of Bichlorinated Methylic Chloride. $C^2HCl^3,2SO^2$.

Sulphite of Perchloride of Carbon, Schwefligsaures Kohlenchlorid, according to Kolbe, who assigns to it the formula, $C^2Cl^3,2SO^2$.—*Methole trichlorosulfuré*, according to Gerhardt, who, with greater probability, expresses its composition by the formula, $C^2HCl^3,2SO^2$.—*Schwefligsaurer trichlorformafer. Gm.*

Discovered and examined by Kolbe in 1845. (*Ann. Pharm.* 54, 153.)

Produced by the action of sulphurous acid, hydrochloric acid, protochloride of tin, or of sulphuric acid with zinc or iron, always in presence of water, on the camphoroidal compound, $CSCl^2O^2 = C^2Cl^4S^2O^4$, discovered by Berzelius & Marcet (II., 337).

Preparation. Sulphurous acid gas is passed through the alcoholic solution of the camphoroidal compound $C^2Cl^4S^2O^4$, till that solution no longer gives a precipitate with water. The camphoroidal compound may also be digested for a considerable time with concentrated sulphurous acid; but the decomposition then takes place more slowly. In both cases, hydrochloric and sulphuric acid are formed at the same time.

This compound, from the great facility with which it decomposes, cannot be obtained in the separate state and analyzed; but Kolbe infers from its mode of formation, that it is composed of C^2Cl^3,S^2O^4:

$$C^2Cl^4S^2O^4 + 2SO^2 + 2HO = C^2Cl^3S^2O^4 + 2SO^2 + 2HCl.$$

But Gerhardt (*N. J. Pharm.* 8, 229) maintains, perhaps with greater reason, that its composition is C^2HCl^3,S^2O^4, and supposes that its formation takes place according to the following equation, which agrees with that of Kolbe, excepting that 1 At. less of HCl is separated. The aqueous or alcoholic solution, after the excess of sulphurous acid has been removed by evaporation, is inodorous and colourless.

$$C^2Cl^4S^2O^4 + 2SO^2 + 2HO = C^2HCl^3S^2O^4 + 2SO^3 + HCl.$$

The aqueous or alcoholic solution thus obtained is colourless and inodorous, after the excess of sulphurous acid has been expelled by heat.

When the solution is exposed to the air, phosgene and sulphuric acid are formed by oxidation; so that when spread out upon a surface, it fills the whole room with the suffocating vapours of these two products (Kolbe):

$$C^2Cl^2S^2O^4 + 4O = 2CClO + 2SO^3.$$

According to Gerhardt's formula, hydrochloric acid must be produced at the same time:

$$C^2HCl^3S^2O^4 + 4O = 2CClO + 2SO^3 + HCl.$$

Chlorine passed into the aqueous solution reprecipitates Berzelius & Marcet's compound (Kolbe):

$$C^2Cl^2S^2O^4 + 2Cl = C^2Cl^4S^2O^4.$$

According to Gerhardt:

$$C^2HCl^3S^2O^4 + 2Cl = C^2Cl^4S^2O^4 + HCl.$$

Bromine forms a similar precipitate, but containing bromine as well as chlorine. (Kolbe.) Iodine forms no precipitate. The aqueous solution boiled with potash, yields the potash-salt of bichlorinated sulphosomethylic acid (Kolbe):

$$C^2Cl^2S^2O^4 + KO + HO = C^2HKCl^2S^2O^6.$$

Or, according to Gerhardt:

$$C^2HCl^3S^2O^4 + 2KO = C^2HKCl^2S^2O^6 + KCl.$$

Kolbe regards this compound, according to his formula, $C^2Cl^2S^2O^4$, as *sulphite of chloride of carbon*, $C^2Cl^2,2SO^4$; Gerhardt, according to the formula which he assigns to it, viz., C^2HCl^3,S^2O^4, regards it as $C^2HCl^3,2SO^2$, that is to say, as a compound of 2 At. sulphurous acid with marsh-gas in which 3H are replaced by 3Cl. Gerhardt's formula may also be written in the form C^2HCl,Cl^2O^2,S^2O^2; according to which it would be a compound of hyposulphurous acid with wood-spirit, in which 3H are replaced by 3Cl.

Terchlorinated Sulphosomethylic Acid. $C^2Cl^3HO^2,2SO^2$.

Chlorkohlen-Unterschwefelsäure (Kolbe), *Acide sulfoformique trichloré* (Laurent), *Acide métholique trichlorosulfuré.*

History, Formation, and *Preparation* (p. 295).

On evaporating the aqueous solution, the acid crystallizes in small

colourless prisms, which, after complete drying in vacuo over oil of vitriol, and afterwards at 100°, form a solid, inodorous, very acid mass, still containing 2 At. water.

Anhydrous acid (unknown) according to Kolbe.

2 C	12·0	.....	6·02
H	1·0	.....	0·50
3 Cl	106·2	.....	53·32
2 S	32·0	.....	16·06
6 O	48·0	.....	24·10
$C^2HCl^3S^2O^6$	199·2	.....	100·00

$C^2Cl^3S^2O^5 + HO$ (Kolbe). $C^2HCl^3,2SO^3$ (Gerhardt).

The hydrated acid fuses at about 130°, begins to boil at 160°, only the smaller portion evaporating undecomposed, while the greater part is resolved into sulphurous acid, hydrochloric acid, and phosgene gases [with evolution of 2 At. water].

$$C^2Cl^3HS^2O^6 = 2SO^2 + HCl + 2CClO.$$

The aqueous acid dissolves zinc, with evolution of gas, forming bichlorinated sulphosomethylate of zinc and chloride of zinc:

$$C^2Cl^3HS^2O^6 + 2Zn \rightarrow C^2Cl^2HZnS^2O^6 + ZnCl.$$

The aqueous solution of the potash-salt, $C^2Cl^3HS^2O^6$, is converted by the electric current, if no free acid is present, into the salt $C^2H^3KS^2O^6$ (p. 295). When the aqueous acid is acted upon by a small quantity of potassium-amalgam (1 pt. potassium to 100 mercury), $C^2Cl^2HKS^2O^6$ is formed; with a larger quantity of the amalgam, $C^2ClH^2KS^2O^6$ is produced, and with a still larger quantity, $C^2H^3KS^2O^6$. These transformations are attended with great evolution of heat and simultaneous formation of potash and chloride of potassium; no hydrogen is evolved till they are completely terminated. (Kolbe.)

The acid is highly deliquescent.

It completely expels the volatile organic acids from their salts, and even decomposes metallic chlorides with evolution of hydrochloric acid. Most of its salts have a harsh metallic taste. At a red heat, they are resolved into metallic chlorides, and equal volumes of sulphurous acid and phosgene gases:

$$C^2Cl^3KS^2O^6 = KCl + 2SO^2 + 2CClO.$$

They are soluble in water and in alcohol. (Kolbe.)

Ammonia-salt.—The aqueous acid neutralized with ammonia yields by spontaneous evaporation large prisms, which are permanent in the air, but when heated are resolved into sal-ammoniac, sulphurous acid and phosgene:

$$NH^3,C^2Cl^3HS^2O^6 = NH^4Cl + 2SO^2 + 2CClO.$$

Potash-salt.—Preparation (p. 297). Purified by re-crystallization. Thin transparent tables having a harsh disagreeable taste; they effloresce in the air, and at 100° give off 7·1 per cent. (2 At.) of water. The salt may be heated to 300° without decomposition; but at a stronger heat, it is decomposed in the manner already mentioned; the residual chloride of potassium is quite free from sulphuric acid.

	Dried at 100°.			Kolbe.
2 C	12·0	5·06		4·90
3 Cl	106·2	44·73		44·70
K	39·2	16·51		16·44
2 S	32·0	13·48		13·20
6 O	48·0	20·22		20·76
$C^2Cl^3KS^2O^6$	237·4	100·00		100·00

Soda-salt.—Obtained like the potash-salt. Thin rhombic tables, which effloresce readily, and are more soluble in water than the potash-salt.

Baryta-salt.—Preparation (p. 296). Crystallizes on cooling from a hot aqueous solution in small colourless laminæ, but by spontaneous evaporation in tables of larger size. The crystals dried at 100° still retain 3·05 per cent. (1 At.) of water, which escapes at 100°.

	Dried at 100°.			Kolbe.
2 C	12·0	4·35		4·35
3 Cl	106·2	38·51		38·70
Ba	68·6	24·87		24·54
2 S	32·0	11·60		
6 O	48·0	17·41		
1 Aq	9·0	3·26		3·37
$C^2Cl^3BaS^2O^6 + Aq$	275·8	100·00		

Lead-salt.—a. Basic.—The aqueous solution of the salt *b*, boiled with oxide of lead, yields an alkaline filtrate, which is precipitated by the carbonic acid of the air, and when evaporated in vacuo, leaves an amorphous saline mass.

b. Neutral.—Crystallizes by spontaneous evaporation of the aqueous solution in broad tables, which redden litmus, and have a sweet, rough taste; they contain 6·1 per cent. (2 At.) of water, which escape at 100°; decomposition begins at 150°.

	Crystallized.			Kolbe.
2 C	12·0	3·75		3·85
3 Cl	106·2	33·17		
Pb	104·0	32·48		32·60
2 S	32·0	9·99		
6 O	48·0	14·99		
2 Aq	18·0	5·62		6·10
$C^2Cl^3PbS^2O^6 + 2Aq$	320·2	100·00		

Copper-salt.—Small tables, permanent in the air and containing 5 At. water, of which only 2 At. go off at 180°, the other three remaining till the salt begins to decompose.

Silver-salt.—The aqueous solution evaporated in vacuo and protected from light, yields transparent and colourless prisms, which redden litmus, have a sweet, metallic taste, blacken on exposure to light, and likewise when their aqueous solution is boiled. But when freed by heating to 100° of the 2 At. water of crystallization which they contain, they remain colourless in sunshine. (Kolbe.)

	Crystals, dried in the air.			Kolbe.
2 C	12·0	3·70		3·55
3 Cl	106·2	32·76		
Ag	108·0	33·31		33·42
2 S	32·0	9·87		
6 O	48·0	14·81		
2 Aq	18·0	5·55		5·77
$C^2Cl^2AgS^2O^6$,2Aq.	324·2	100·00		

With regard to the formulæ which should be assigned to the acids, $C^2H^4S^2O^6$—$C^2H^3ClS^2O^6$—$C^2H^2Cl^2S^2O^6$, and $C^2HCl^3S^2O^6$, *vid.* besides Kolbe, also Berzelius (*Pogg.* 68, 185), Laurent (*Compt. rend.* 21, 36), and Gerhardt (*N. J. Pharm.* 8, 229). The formulæ which I have proposed are supported by the fact that in the decompositions of these acids and their salts, sulphurous acid is evolved, but no sulphuric acid separated.

f. Secondary Nucleus. C^2Cl^2.

Terchlorinated Methyl-Ether. C^2Cl^2,ClO.

Regnault (1839). *Ann. Chim. Phys.* 71, 396; also *Ann. Pharm.* 31, 29; also *J. pr. Chem.* 19, 271.

Ether methylique perchloruré, Trichlorformäther [*Nakaformek*].

Formed by the action of chlorine gas on monochlorinated methyl-ether, C^2H^2ClO, first in bright daylight, then in sunshine, whereby it is converted, first into C^2HCl^2O, then into C^2Cl^2O, part of which, in consequence of its volatility, is carried forward by the chlorine gas.

Liquid; sp. gr. 1·594; boiling point about 100°; vapour-density = 4·670; odour extremely suffocating.

When this compound is treated with chlorine in sunshine for two days, a liquid is formed containing 90·5 per cent. of carbon and 85·11 of chlorine. Hence the chlorine appears ultimately to expel even the oxygen [in the form of oxygen gas ?] and to produce C^2Cl^4. (Regnault.)

			Regnault.		Vol.	Density
2 C	12·0	9·51	9·55	C-vapour	2	0·8320
3 Cl	106·2	84·15	83·62	Cl-gas	3	7·3629
O	8·0	6·34	6·68	O-gas	½	0·5546
H			0·15			
C^2Cl^2,ClO	126·2	100·00	100·00		2	8·7495
					1	4·3748

Whilst, therefore, the vapours of C^2H^2O, C^2H^2ClO, and C^2HCl^2O are monatomic, that of C^2Cl^2O is diatomic. Connected with this, is the apparent anomaly that the specific gravity and boiling point of C^2Cl^2O are only 1·594 and 100°, whereas those of C^2HCl^2O are 1·606 and 130°. A great alteration must therefore have taken place in the relative position, of the atoms, whereby the character of the ether (that, namely, of forming a monatomic vapour) has been destroyed, and at the same time the specific gravity and boiling point, instead of being raised (by the substitution of Cl for H) have actually been lowered. According to this view, Kopp's

suggestion (*Ann. Pharm.* 41, 176) that Regnault's determinations of the specific gravity and boiling point of this compound are incorrect, does not appear to be well founded.

¶ According to Gerhardt's views, if the vapour be really diatomic, the numbers of atoms of Cl and O in the formula should be divisible by 2. Gerhardt therefore suggests, that the compound C^2Cl^2O may be resolved by heat into CClO and CCl^2 (the corresponding ethyl-compound C^4Cl^6O is decomposed in a similar manner); that the vapour whose density was determined by Regnault, was actually a mixture of those two gases in equal volumes—a supposition which agrees very well with Regnault's determination—and that the boiling-point determined by Regnault is really the temperature at which decomposition takes place. ¶

Terchlorinated Methylic Sulphide. C^2Cl^3,ClS.

REGNAULT. *Ann. Chim. Phys.* 71, 408; also *Ann. Pharm.* 34, 36; also *J. pr. Chem.* 19, 279.

Schwefel-Trichlorformafer, Ueberchlorhaltiger Schwefelwasserstoffäther; Éther hydrosulfurique de methylène perchloruré, Sulfure de methyle perchloruré [*Fakaformek*].

When chlorine gas is passed into a glass globe containing sulphide of methyl, C^2H^3S, and kept cool at the beginning of the action, there is gradually formed a yellow oily stratum of liquid, which goes on increasing, whilst the colourless layer diminishes and gradually disappears. The product formed at this stage of the operation is probably C^2HCl^3S, *éther hydrosulfurique de l'esprit de bois monochloruré;* but it decomposes on being subjected to distillation. If this yellow oil be placed in a bottle filled with dry chlorine and exposed to the sun till it is no longer acted upon by the chlorine, it is converted, without further formation of hydrochloric acid, into the stinking liquid which, when purified by distillation, is the compound C^2Cl^3S. (Regnault.)

				Regnault.
C	12·0	....	8·94	8·40
3 Cl	106·2	....	79·14	
S	16·0	....	11·92	
H		....		0·17
C^2Cl^3,ClS	134·2	....	100·00	

Bichloride of Carbon. C^2Cl^3,Cl^3.

REGNAULT. *Ann. Chim. Phys.* 71, 377; also *Ann. Pharm.* 33, 328; also *J. pr. Chem.* 19, 210.
DUMAS. *Ann. Chim. Phys.* 73, 95.
KOLBE. *Ann. Pharm.* 45, 41 and 54, 146.

Kohlensuperchlorid (Kolbe), *Ether hydrochlorique perchloruré* (Regnault), *Formène perchloruré* (Gerhardt), [*Keformek*].—Discovered by Regnault in 1839.

Formation and *Preparation*. 1. *Marsh-gas decomposed by Chlorine:*

$$C^2H^4 + 8Cl = C^2Cl^4 + 4HCl.$$

A bottle of the capacity of 1 litre, filled with marsh-gas, is inverted over another having a capacity of 3 [4] litres, filled with chlorine; the mouths connected by a narrow tube luted with clay, and the whole exposed to the sun's rays. By this arrangement, the gases are made to mix and act upon each other very slowly, and all risk of explosion is avoided. The oil hereby condensed is freed by rectification from chloroform, which being lighter passes over first. (Dumas.)—2. *Chloroform decomposed by Chlorine:*

$$C^2HCl^3 + 2Cl = C^2Cl^4 + HCl.$$

Chloroform is gently heated in a retort attached to a receiver and exposed to the sun, and a stream of dry chlorine gas passed slowly but continuously through the tubulus. The liquid which distils over is repeatedly poured back, and the process continued till hydrochloric acid ceases to be evolved; after which the distillate is agitated with mercury to remove free chlorine, and then distilled again. (Regnault.)—3. *Sulphide of Carbon decomposed by Chlorine:*

$$C^2S^4 + 8Cl = C^2Cl^4 + 4SCl.$$

Perfectly dry chlorine is passed first through a bottle (not heated) containing sulphide of carbon, the vapour of which mixes with the chlorine, and then through a porcelain tube filled with fragments of porcelain and kept at a bright-red heat. In the receiver, which must be well cooled, a yellowish-red liquid collects, which is a mixture of bichloride of carbon and chloride of sulphur, weighing considerably more than the sulphide of carbon which has evaporated. This liquid is added, so slowly as not to produce rise of temperature, to an excess of potash-ley or milk of lime, the mixture set aside and agitated, from time to time, till the chloride of sulphur is decomposed, and then distilled. Chloride of carbon then passes over, either pure, or mixed with sulphide of carbon, if too much of that compound has evaporated in the chlorine gas, or if the heat has not been sufficiently strong. The sulphide of carbon is best removed by placing the mixture for some time in contact with potash-ley. (Kolbe.)

Properties. Thin, transparent, and colourless oil, of sp. gr. 1·599 (Regnault), 1·56 (Kolbe). Boils at 78° (Regnault), at 77° (Kolbe). Vapour-density 5·330 (Regnault), 5·24 (Kolbe). Smells like sesquichloride of carbon, C^4Cl^6 (Regnault); has a pleasant aromatic odour. (Kolbe.)

			Regn.	Dumas.	Kolbe.		Vol.	Density.
2 C	12·0	7·81	7·83	7·94	7·85	C-vapour	2	0·8320
4 Cl	141·6	92·19		91·90	92·00	Cl-gas	4	9·8172
H	....	....	....	0·16				
C^2Cl^4	153·6	100·00		100·00	99·85	C^2Cl^4-vapour	2	10·6492
								5·3246

The vapour of this compound repeatedly passed through a tube kept at a bright red heat and filled with fragments of glass, is for the most part resolved into chloride of carbon, C^2Cl^4, and free chlorine; at a still higher temperature, crystals of Julin's compound, C^4Cl^2, are produced. If, on the contrary, the tube is only at a dull-red heat, the product is ses-

quichloride of carbon, which, however, is probably not Faraday's compound, C^4Cl^6, but an isomeric body, C^2Cl^3, inasmuch as its vapour-density appears to be only 4·082. (Regnault.) According to Kolbe, the vapour is decomposed in the red-hot tube into chlorine gas, and a liquid mixture of CCl [C^4Cl^4] and C^2Cl^3 [C^4Cl^6], which, by the action of dry chlorine in sunshine, is almost instantly converted into the solid sesquichloride, C^2Cl^3 [C^4Cl^6].—Bichloride of carbon burns in the flame of a spirit-lamp, forming vapours of hydrochloric acid. (Kolbe.)—Its vapour passed, together with sulphuretted hydrogen gas, through a glass tube at a low red heat, is converted into sulphide of chloride of carbon and hydrochloric acid. (Kolbe.)

$$C^2Cl^4 + 2HS = C^2Cl^2S^2 + 2HCl.$$

It is not decomposed by aqueous solution of potash, and but slowly by the alcoholic solution, with separation of chloride of potassium and carbonate of potash. (Kolbe.) It may likewise be distilled without decomposition, over an alcoholic solution of sulphide of hydrogen and potassium. (Regnault.)

Sulphide of Chloride of Carbon. C^2Cl^2,S^2.

KOLBE. *Ann. Pharm.* 45, 43;—54, 147.

Formation and *Preparation*. 1. A few grammes of sulphide of carbon are placed in a closed capacious bottle filled with dry chlorine, and left for some time, either in the dark or exposed to the sun. The chlorine condenses with the sulphide of carbon into a reddish yellow liquid, a mixture of sulphide of chloride of carbon and chloride of sulphur. Water is added to decompose the latter, and the sulphide of chloride of carbon is repeatedly distilled over magnesia and water, to free it from adhering acid. (When a few drops of sulphide of carbon are placed in contact with dry chlorine gas, they evaporate, and afterwards condense into a dark red liquid, which is a mixture of bichloride of carbon and chloride of sulphur; but if a trace of water be present, Berzelius & Marcet's camphoroidal compound is produced instead of this. (Kolbe, *Ann. Pharm.* 54, 148.) This last statement respecting the action of dry chlorine appears to contradict the first.)—2. Sulphide of carbon is placed, together with the mixture of hydrochloric acid and manganese for evolving chlorine, in a closed vessel for several weeks, the mixture being frequently agitated, and then the compound is distilled off. [By the same method (*Ann. Pharm.* 54, 152), Kolbe prepares Berzelius and Marcet's camphoroidal compound: wherein consists the difference of the treatment?]—3. Vapour of bichloride of carbon, mixed with sulphuretted hydrogen, is passed through a glass tube, kept at a moderate red heat:

$$C^2Cl^4 + 2HS = C^2Cl^2S^2 + 2HCl.$$

Yellow oil, of sp. gr. about 1·46; boils at about 70°, has a powerful odour, and attacks the eyes strongly,

			Kolbe (*approximate*).
2 C	12·0	10·45	10·72
2 Cl	70·8	61·67	56·76
2 S	32·0	27·88	32·16
$C^2Cl^2S^2$	114·8	100·00	99·64

Kolbe is of opinion that the liquid which he analyzed still contained sulphide of carbon. The compound may be regarded as phosgene, in which the oxygen is replaced by sulphur. (Kolbe.) It is slowly decomposed by potash-ley, with formation of carbonate of potash and sulphide of potassium, and deposition of colourless oily bichloride of carbon. Water, fuming nitric acid, and other acids, exert no action upon it.

This compound is probably nothing more than a variable mixture of C^2Cl^4 and CS^2? (Gm.)

Copulated Compounds.

Berzelius & Marcet's Camphoroidal Compound. C^2Cl^4,S^2O^4.

KOLBE. *Ann. Pharm.* 54, 128.

Sulphite of Perchloride of Carbon, *Schwefligsaures Kohlensuperchlorid* (Kolbe), *Methyle quadrichlorosulfuré* (Gerhardt).

This compound has been already described among inorganic compounds (II. 337), under the name of *Carbonate of Bichloride of Sulphur*. But as the latter experiments of Kolbe have rendered it highly probable that it is of organic nature, and, moreover, Kolbe has communicated several new facts respecting it, a further description of it may properly be given in this place.

This body is formed by the action of moist chlorine on bisulphide of carbon. The chlorine first forms bichloride of carbon and protochloride of sulphur:

$$CS^2 + 4Cl = CCl^2 + 2SCl;$$

and this chloride of sulphur is then decomposed by the water, yielding sulphurous acid, sulphur, and hydrochloric acid, the sulphurous acid remaining in combination with the CCl^2:

$$CCl^2 + 2SCl + 2HO = CCl^2SO^2 + S + 2HCl.$$

We cannot, however, produce this compound by the direct combination of bichloride of carbon, prepared in the separate state, with sulphurous acid. (Kolbe.) [The equation taken twice is,

$$C^2S^4 + 8Cl = C^2Cl^4 + 4SCl;$$

then:

$$C^2Cl^4 + 4SCl + 4HO = C^2S^2Cl^4O^4 + 4HCl + 2S.]$$

Preparation (Kolbe, II., 337, 2).

Properties. This body sublimes in the bottles in which it is kept, in transparent, colourless, rhombic tables, having an adamantine lustre, and often truncated on the acute lateral edges, the angles of which do not differ much from 60°, so that nearly regular hexagonal prisms are produced. Begins to melt at 135°, boils at 170°, and may be volatilized undecomposed, either alone or with water. Vapour-density 7·430. The vapour has a pungent odour, excites tears, and when inhaled in rather large quantity, produces intolerable irritation in the throat, but does not otherwise injure the health. (Kolbe, *comp.* II., 337, 338.)

			Kolbe.			Vol.	Density.
2 C	12·0	5·51	5·4	C-vapour	2	0·8320
2 S	32·0	14·71	14·9	S-vapour	½	2·2186
4 Cl	141·6	65·07	65·1	Cl-gas	4	9·8172
4 O	32·0	14·71	14·6	O-gas	2	2·2186
$C^2S^2Cl^2O^4$	217·6	100·00	100·0		2	15·0864
					1	7·5432

The vapour of the compound passed through a glass tube at a dull red heat, is resolved into bichloride of carbon and sulphurous acid. (Kolbe.) Heated with oil of vitriol it yields phosgene-gas, hydrochloric acid, and sulphurous acid (Kolbe):

$$CCl^2,SO^2 + HO,SO^2 = CClO + HCl + SO^2 + SO^2.$$

or, doubled:

$$C^2Cl^4S^2O^4 + 2(HO,SO^2) = 2CClO + 2HCl + 2SO^2 + 2SO^2.$$

In contact with air and water it is slowly resolved into carbonic, hydrochloric, sulphurous, and sulphuric acid, the latter produced by the air. Hence it reddens litmus when moistened. (Kolbe.) When suspended in water, it is slowly, but in the state of alcoholic solution, quickly decomposed by sulphurous acid, yielding sulphite of protochloride of carbon, hydrochloric acid, and sulphuric acid:

$$CCl^2,SO^2 + HO + SO^2 = CCl,SO^2 + HCl + SO^2;$$

or, according to Gerhardt (p. 351):

$$C^2Cl^4S^2O^4 + 2HO + 2SO^2 = C^2HCl^3S^2O^4 + HCl + 2SO^2.$$

Sulphuretted hydrogen acts on the alcoholic solution in a similar manner, producing, however, a precipitate of sulphur:

$$CCl^2SO^2 + HS = CClSO^2 + HCl + 2S.$$

according to Gerhardt's view:

$$C^2Cl^4S^2O^4 + 2HS = C^2HCl^3S^2O^4 + HCl + 2S.$$

Aqueous protochloride of tin dissolves the compound with great evolution of heat, forming a liquid which contains sulphite of protochloride of carbon and bichloride of tin:

$$CCl^2SO^2 + SnCl = CClSO^2 + SnCl^2;$$

according to Gerhardt, perhaps:

$$2C^2Cl^4S^2O^4 + 4SnCl + 2HO = 2C^2Cl^3HS^2O^4 + 3SnCl^2 + SnO^2.$$

In fact, if the solution of protochloride of tin does not contain free hydrochloric acid, the mixture yields a white precipitate, even when the air is excluded. (Gm.)

Zinc or iron brought in contact with the compound dissolved in very dilute, slightly acidulated alcohol, likewise produces sulphite of protochloride of carbon:

$$CCl^2SO^2 + Zn = CClSO^2 + ZnCl;$$

according to Gerhardt's view:

$$C^2Cl^4S^2O^4 + HO + 2Zn + SO^2 = C^2HCl^3S^2O^4 + ZnCl + ZnO,SO^2.$$

Lastly, the compound is converted into the sulphite of protochloride

of carbon by the action of the electric current, the change being most easily produced by the use of two electrodes of amalgamated zinc.

The compound heated with aqueous potash, is resolved into terchlorosulphosomethylate of potash and chloride of potassium (a small quantity of sulphuric acid is obtained at the same time, having been previously formed in the moist compound by exposure to the air): $C^2Cl^4S^2O^4 + 2KO = C^2Cl^3KS^2O^6 + KCl$.

g. Secondary Nucleus. C^2X^2 ($C^2N^2O^6$).

Chloride of Binitromethylene. C^2X^2,Cl^2.

Marignac (1841). *Ann. Pharm.* 38, 14.

[*Reformert.*]—The compound $C^{20}H^8,Cl^4$ [*Konofite*], is distilled with concentrated nitric acid, till nearly all the acid has passed over, and the acid distillate, from which part of the new product has settled down in the form of an oil having a pungent odour, is again distilled; the oil then passes over first. It is washed, and afterwards distilled with water.

Transparent, colourless liquid, of specific gravity 1·685 at 15°. By itself it does not boil till heated above 100°, but when distilled with water, it passes over at the beginning with a portion of the water. Neutral towards vegetable colours. Has a very pungent odour, like that of chloride of cyanogen; its vapour attacks the eyes powerfully.

Does not act upon mercury at ordinary temperatures, but when heated with that metal, covers it with a film of calomel, and is converted into a vapour, which is resolved, with slight explosion, into chlorine, nitric oxide, and carbonic acid gas.—Insoluble in aqueous potash, but dissolves readily in alcoholic potash; the solution then deposits a potash-salt, which detonates when heated.—Almost insoluble in water, sparingly soluble in nitric or hydrochloric acid; dissolves easily in alcohol and ether. (Marignac.)

				Marignac.
2 C	12·0	6·87		7·04
2 N	28·0	16·02		16·29
8 O	64·0	36·61		35·84
2 Cl	70 8	40·50		40·83
C^2X^2,Cl^2	174·8	100·00		100·00

h. Secondary Nucleus. C^2Ad^2 ($C^2N^2H^4$).

Urea. $C^2N^2H^4O^2 = C^2Ad^2,O^2$.

Fourcroy & Vauquelin. *Ann. Chim.* 32, 80; also *Crell, Ann.* 1800, 1, 149 and 30, 244 and 342.—*Ann. du Mus.* 2, 226; also *N. Gehl.* 6, 409.

Proust. *J. Phys.* 56, 113; also *A. Gehl.* 3, 332.—*Ann. Chim. Phys.* 14, 265.

Vauquelin. *Ann. Chim. Phys.* 25, 423; also *Schw.* 42, 52.

Pfaff. *Schw.* 5, 162.

PROUT. *Ann. Phil.* 11, 352; also *Ann. Chim. Phys.* 20, 369; abstr. *Schw.* 22, 449.
WÖHLER. *Pogg.* 12, 253; 15, 619.
LIEBIG & WÖHLER. *Pogg.* 20, 372.
MORIN. *Ann. Chim. Phys.* 61, 5.
DUMAS. *Ann. Chim. Phys.* 44, 273; also *Schw.* 61, 98; also *Pogg.* 19, 487.
O. HENRY & CAP. *J. Pharm.* 25, 133.
PELOUZE. *N. Ann. Chim. Phys.* 6, 65; also *Ann. Pharm.* 44, 102; also *J. pr. Chem.* 28, 18.
R. F. MARCHAND. *J. pr. Chem.* 34, 248; 35, 481.—*Pogg.* 66, 118 and 317.
W. HEINTZ. *Pogg.* 66, 118; 67, 104; *J. pr. Chem.* 42, 401.
WERTHER. *J. pr. Chem.* 35, 51.
BUNSEN. *Ann. Ch. Pharm.* 65, 375; *Pharm. Centr.* 1848, 117; *N. J. Pharm.* 16, 151; *Jahresber.* 1847–8, 989.
MILLON. *Compt. rend.* 26, 119; *Pharm. Centr.* 1848, 189; *Jahresber.* 1847–8, 991.
GLADSTONE. *Ann. Pharm.* 66, 1; *Pharm. Centr.* 1848, 637; *Jahresber.* 1847–8, 488.

Harnstoff, Urenoxyd-Ammoniak, Urée.—Obtained in an impure state as *Extractum Saponaceum Urinæ* by Rouelle the younger in 1773; afterwards prepared in a state of greater purity by Fourcroy & Vauquelin in 1799.

Sources. In human urine, in the free state, to the amount of 2 to 4 per cent.* In the urine of all mammalia, being particularly abundant in that of the carnivora. In small quantity in the urine of all carnivorous birds (Coindet), of the goose (J. Davy), of the dove and canary-bird; also in that of the boa (Cap & O. Henry, *J. Pharm.* 25, 137); more abundantly in the urine of toads and frogs. (J. Davy.) The statements of Persoz (*Chim. moléculaire*) and of Morin, that urea does not exist ready formed in urine, but is produced only under certain circumstances; and of O. Henry & Cap, that it is combined, in the urine of man, with lactic acid; in that of herbivorous quadrupeds, with hippuric acid; and in that of birds and serpents, with uric acid—have been disproved by Lecanu (*Ann. Chim. Phys.* 74, 90; also *J. pr. Chem.* 21, 302), and by Pelouze (*N. Ann. Chim. Phys.* 6, 66).†—2. In the blood of dogs, after the extirpation of their kidneys. (Prevost & Dumas, *Ann. Chim. Phys.* 23, 90; Vauquelin & Ségalas, *Magendie, J. de Physiol.* 2, 354; Mitscherlich, Tiedmann & Gm. *Pogg.* 31, 303.) In the blood of a sheep whose renal

* Millon states that in healthy human urine there is a certain correspondence between the specific gravity and the per-centage of urea, the second and third digits in the sp. gr. (A) nearly expressing the quantity of urea contained in 1000 parts of urine (B): thus, the sp. gr. being taken at 15°:

A	1·0116	1·0046	1·0092	1·0277	1·0143	1·0110	1·0260	1·0290
B	11·39	4·39	9·88	29·72	11·99	10·60	25·80	31·77

No such correspondence is found in the urine of the lower animals, or in that of man in a state of disease or when the mode of living is somewhat disturbed. (*Compt. rend.* 26, 120; *Pharm. Centr.* 1848, 189; *Jahresber.* 1847–8, 925.) [W.]

† Liebig also finds that lactic acid does not occur in urine, either fresh or putrid, not even after the introduction of lactate of potash into the system. (*N. Ann. Chim. Phys.* 23, 358.) [W.]

nerves had been tied (even the blood which issued on the last day of the animal's life was found to be rich in urea). (Marchand, *J. pr. Chem.* 11, 455.) In the blood of cholera patients, when they have not voided any urine for several days. (Marchand, *Pogg.* 44, 328; *J. pr. Chem.* 11, 449.) Also in that of patients suffering from *albuminuria*. (Garrod, *Transac. med. chir.* 31, 83.) In the blood of a healthy cow, cognizable only by the octahedral crystallization of the chloride of sodium mixed with it. (Marchand, *J. pr. Chem.* 14, 490; *comp.* also Prout, *Lond. Med. Gas.* 1831, June; also *Froriep's Notizen*, 32, 22.) Verdeil & Dollfus (*Compt. rend.* 30, 657) likewise found it in ox-blood.—3. In the liquid of a *Hydrocele* (Marchand, *J. pr. Chem.* 14, 490); in the dropsical fluid of three patients suffering from *Ascites*, in whom great retention of urine had taken place, the proportion being ½ per cent. (Marchand, *Pogg.* 38, 356; and *Müller's Arch. J. Physiol.* 1837, 440.)—4. In the human *liquor amnii*. (Wöhler, *Ann. Pharm.* 58, 98.) ¶ J. Regnauld, (*Compt. rend.* 31, 218), found in the amniotic liquid of women about 1·2 per cent. of solid constituents, and among them urea, which was recognized by evaporating the liquid at 100° to one-third of its bulk, then to dryness in vacuo over oil of vitriol, exhausting the residue with alcohol, evaporating to dryness, and dissolving out the urea from the residue with ether.—4. Stas (*Compt. rend.* 31, 629) found urea in the allantoic liquid of women; also in the blood of the placenta, the liquid part of which consists almost wholly of casein.—5. In the eye, according to Millon (*Compt. rend.* 26, 121). The residue left on evaporating to dryness the vitreous humour of the eyes of oxen (which residue amounts to 1·63 per cent. of the liquid) contains from 20 to 35 per cent. of urea, the remaining portion appearing to consist entirely of chloride of sodium. The vitreous humour of man and of the dog has the same composition. The aqueous humour likewise contains urea and chloride of sodium. ¶

Formation. 1. Aqueous cyanic acid, C^2NH,O^2, combines with aqueous ammonia, forming cyanate of ammonia, which, even at ordinary temperatures, yields cyanic acid when treated with acids, and ammonia when treated with potash. But when this compound is heated or abandoned to spontaneous evaporation, the atoms unite in the form of a new substance, which no longer exhibits the preceding reactions (Wöhler), $NH^3,C^2NHO^2 = C^2H^4N^2O^2$. Hence, also, urea is produced on evaporating cyanate of lead with aqueous carbonate of ammonia, or cyanate of silver with aqueous sal-ammoniac, inasmuch as in either of these cases, cyanate of ammonia is formed by double decomposition. Similarly, the aqueous solution of cyanogen yields urea by spontaneous decomposition, cyanate of ammonia being formed in the first stage of the process, and afterwards converted into urea as the liquid evaporates. (Wöhler.) If the formula of urea be $C^2Ad^2O^2$, we must suppose that not only the nitrogen of the ammonia, but likewise that of the cyanic acid is converted into amidogen. ¶ Fulminate of copper and ammonia decomposed by sulphuretted hydrogen, likewise yields urea.—1 At. fulminate of copper and ammonia and 3 At. sulpuretted hydrogen, yield 1 At. sulphide of copper, 1 At. urea, 1 At. hydrosulphocyanic acid, and 2 At. water:

$$C^4N^2O^2,NH^4O,CuO + 3HS = CuS + C^2N^2H^4O^2 + C^2NS^2H + 2HO.$$

(Gladstone, *Ann. Pharm.* 66, 1.) The possibility of this transformation was first suggested by Liebig. (*Lancet*, Dec. 1844.) ¶—2. Oxaluric acid

boiled for a long time with water is resolved into urea and oxalic acid. (Liebig.)—3. Uric acid subjected to dry distillation (Wöhler), or to the oxidizing action of peroxide of lead, bichromate of potash, or nitric acid, yields urea, together with other products of decomposition. (Liebig & Wöhler.) Also when oxidized by permanganate of potash. (Gregory.)—4. Oxamide passed in the state of vapour through a glass tube heated to redness for the length of 2 inches, yields, among other products, a large quantity of urea.

Preparation. 1. The urine of man [or better, that of lions or tigers, which yields the urea in larger quantity and less coloured] is evaporated, first over the open fire, and then in the water-bath, to the consistence of honey; the residue boiled with a fourfold quantity of alcohol of 36° Bm.; part of the alcohol separated from the filtrate by distillation; the solution left to cool, and the urea which separates, purified by repeated crystallization from water, or better from alcohol. (Fourcroy & Vauquelin.)

2. *a.* Urine evaporated to the consistence of a thin syrup is mixed with an equal volume of nitric acid of 24° Bm.; the mixture surrounded with ice for several hours; the liquid decanted from the precipitated nitrate of urea; the precipitate washed on a filter with a small quantity of ice-cold water; well pressed between bibulous paper; dissolved in luke-warm water; decomposed by neutralizing the acid with carbonate of potash; evaporated; and the urea separated from the nitre by alcohol of 40° Bm. from which the urea crystallizes on evaporation. (Fourcroy & Vauquelin.)—*b.* Prout pours upon the nitrate of urea prepared according to (2. *a*), a quantity of a concentrated solution of carbonate of potash sufficient to render the liquid perfectly neutral; then evaporates and cools the solution; decants the liquid from the nitre which has crystallized out; mixes it with enough animal charcoal to make it into a paste; washes this after a few hours with water; filters; evaporates slowly to dryness; boils the colourless residue with alcohol; filters to separate the nitre and other salts; and crystallizes the urea several times from alcohol.—*c.* Morin digests the nitrate of urea prepared by (2. *a*), which still retains a yellow tint from the colouring matter of the urine, with water and crude bone charcoal; filters; and adds carbonate of potash to precipitate the lime dissolved out from the bones; evaporates the filtrate to the consistence of a syrup, which crystallizes on cooling; boils the residue with alcohol of 40° Bm.; filters the liquid; leaves it to cool; and crystallizes the resulting crystals once more from alcohol.—*d.* Knörzer (*J. Scienc. physiq.* 4,176) mixes the evaporated urine in the cold with an equal volume of nitric acid of 33° Bm , and proceeds with the rest of the process in the same manner, excepting that he finally digests the urea in the state of aqueous solution with the precipitate obtained by adding carbonate of potash to subacetate of lead. The crystals thereby obtained are colourless. In winter, according to Knörzer, the urine may be concentrated by freezing instead of evaporation.—*e.* Proust boils the nitrate of urea obtained by (2. *a*) with white lead and water; filters and evaporates, whereupon nitrate of lead crystallizes out; precipitates the remainder of that salt by addition of alcohol; filters; distils off the alcohol; removes the yet remaining lead by hydrosulphuric acid; filters again; and leaves the urea to crystallize.—*f.* The nitric acid must be free from nitrous acid, which would decompose the urea. If the precipitated nitrate of urea is coloured, it cannot well be purified by animal charcoal. It is better in

that case to separate the urea from it, and reprecipitate by nitric acid. The nitrate of urea must then be digested with water and carbonate of baryta, the solution evaporated, and the urea extracted from the residue by alcohol of medium temperature, because hot alcohol would also take up a small quantity of nitrate of baryta. (Wöhler.)—*g.* Instead of precipitating the syrup obtained by evaporating the urine with nitric acid in the cold, it may be precipitated hot; in that case, instead of the coloured crystals, colourless crystals will be obtained in equally large quantity; for urea is but little decomposed by nitric acid, even when hot. (Cap & Henry.)—*h.* The decoloration of nitrate of urea is best effected by distilling 1 pt. of it with 3 pts. of a mixture of 1 vol. colourless nitric acid, of sp. gr. 1·401, and 2 vol. alcohol of 35° Bm., till crystals of nitrate of urea begin to form on the surface of the residual solution. Nitric ether passes over in the distillation. (Millon, *N. Ann. Chim. Phys.* 8, 235.)

3. The evaporated urine is dried as completely as possible in the water-bath; the residue completely exhausted with absolute alcohol; the alcohol distilled off from the filtrate; the yellow residue dissolved in a small quantity of water; the solution digested with a small quantity of the charcoal obtained in the preparation of ferrocyanide of potassium (*Blutlaugenkohle*), whereby it is nearly decolorized; and the filtrate saturated at 50° with crystallized oxalic acid. The liquid, on cooling, yields colourless crystals of oxalate of urea. If the liquid be heated to 100°, it becomes dark brown, acquires a bad odour, and yields red-brown crystals; which, however, may be decolorized by charcoal obtained from the preparation of ferrocyanide of potassium. The mother-liquid gently evaporated, and, if necessary again mixed with oxalic acid, yields an additional crop of crystals. The whole of the crystals, after being freed from the mother-liquid by a small quantity of ice-cold water, are dissolved in boiling water; and the solution, mixed with a small quantity of the animal charcoal above-mentioned, then digested, filtered, and cooled, yields oxalate of urea in snow-white crystals. The mother-liquor, if further evaporated and cooled, crystallizes to the last drop, and at first yields an additional quantity of colourless crystals. The colourless crystals are dissolved in boiling water; the solution mixed with very finely pounded carbonate of lime till it no longer reddens litmus; then filtered and evaporated; and from the dried residue, which likewise contains small quantities of oxalate of ammonia, potash or soda, the urea is extracted by absolute alcohol. (Berzelius, *Pogg.* 18, 84.)

4. *a.* O. Henry (*J. Pharm.* 15, 161) mixes the fresh urine with excess of subacetate or hydrated oxide of lead; pours off the liquid from the precipitate; adds to it enough sulphuric acid to precipitate the lead, and convert the acetates into sulphates; mixes the filtrate with animal charcoal; boils it rapidly; strains the thin syrup through a thick linen cloth; evaporates the filtrate further by one-third; cools it, whereupon it solidifies in a yellow crystalline mass; subjects this mass to pressure; endeavours by further evaporation, cooling, and pressure, to obtain more crystals from the expressed mother-liquid; treats the whole of the crystals with a small quantity of carbonate of soda, to decompose any acetate of lime that may be present and would dissolve in alcohol; then digests them with alcohol of 40° Bm.; distils off the alcohol from the filtrate, and purifies the crystals thus obtained, by once more dissolving them in water and crystallizing. The urea obtained by this process is at most contaminated with a trace of chloride of sodium, whereas that which is prepared by (2) is apt to contain nitrate of potash or ammonia.—

b. Morin precipitates the evaporated urine with subacetate of lead; throws down the lead from the filtrate by sulphuretted hydrogen; filters and evaporates; exhausts the residue with boiling alcohol; evaporates the filtrate to dryness; dissolves the residue in water; precipitates by nitric acid; and treats the nitrate of urea by one of the preceding methods.

5. Cyanide of potassium is prepared by fusing the ferrocyanide with carbonate of potash, and thence, by fusion with litharge, cyanate of potash (*q. v.*) is obtained. The cyanate, without further purification, is dissolved in water; an aqueous solution of sulphate of ammonia added [about equal parts of the two]; the mixture evaporated over the water-bath, and freed, as far as possible, from the crusts of sulphate of potash which form upon it; and the dried residue finally obtained is boiled with alcohol of 80 or 90 per cent. The solution filtered from the rest of the sulphate of potash, yields by cooling and further evaporation of the mother-liquid, colourless crystals of urea, amounting to ½ of the ferrocyanide of potassium used. (Liebig, *Ann. Pharm.* 38, 108; 41, 289.) This is the most productive and the cleanest method of preparing urea.—¶ According to Clemm (*Ann. Pharm.* 61, 250), the cyanate of potash is best prepared by gradually adding 15 parts of red lead to the fused and somewhat cooled but still liquid mixture of 8 pts. ferrocyanide of potassium and 3 pts. carbonate of potash, especial care being taken that the temperature do not rise too high. The crucible is then again put into the fire, and the mixture stirred, poured out, and left to cool. To obtain urea from this product, it must be immediately digested and washed in cold water; sulphate of ammonia (8 pts. for the above proportions) dissolved in the last wash-water; the mixed solutions evaporated, and the process completed as usual. Any ferrocyanide of potassium that may be present in the alcoholic solution is easily removed by carefully adding ferric sulphate, and decanting the solution from the Prussian blue thereby produced. By this process, 8 pts. ferrocyanide of potassium yield from 4 to 5 pts. of urea. ¶

Properties. Transparent, colourless prisms, needles and laminæ (sometimes yellow or brownish from impurities). Square prisms, sometimes perpendicularly truncated, sometimes bevelled with two faces resting on two of the opposite lateral faces at one end, and on the two other lateral faces at the other end. (Werther.)—Urea which crystallizes, not in prisms but in laminæ, is impure, and leaves an alkaline residue when ignited. (Wöhler.)—Sp. gr. 1·35. (Proust.) The aqueous solution of urea does not exhibit circular polarization, and is thereby distinguished from the natural alkaloids. (Biot.)—Fuses at about 120°. (Wöhler.) Inodorous (it is only when impure that it smells like urine). Has a sharp cooling taste, and exerts a diuretic action. Exhibits neither acid reaction on litmus, nor alkaline on violet juice.

	Crystallized.		Prout.	Liebig & Wöhler.	Bérard.	Prevost & Dumas.
2 C	12	20·00	19·98	20·02	18·9	18·23
4 H	2	6·67	6·65	6·71	9·7	9·89
2 N	28	46·67	46·65	46·73	45·2	42·23
2 O	16	26·66	26·72	26·54	26·2	29·65
$C^2Ad^2O^2$	60	100·00	100·00	100·00	100·0	100·00

O. Henry (*J. Pharm.* 19, 18) obtained 46·61 per cent. of nitrogen. Varrentrapp & Will (*Ann. Pharm.* 39, 278) obtained 46·79.—Crystal-

lized urea loses nothing at 100° (Liebig & Wöhler); the 2 per cent. of water which, according to Vauquelin, it gives off in vacuo over oil of vitriol, was probably due to hygroscopic moisture and adhering mother-liquid.—The urea analyzed by Prévost & Dumas (*J. Phys.* 95, 218) was obtained from the blood of a dog whose kidneys had been extirpated. If urea be regarded as $C^2Ad^2O^2$, a view which is supported by its reactions with oil of vitriol, potash, and water, we must suppose it to be formed from an unknown bibasic acid, $C^2H^2O^6$; for,

$$C^2H^2O^6 + 2NH^3 - 4HO = C^2H^4N^2O^4;$$

just as oxalic acid, $C^4H^2O^8$, with 2 At. ammonia, yields oxamide, $C^4H^4N^2O^4$ and 4HO. At all events urea cannot, for the reasons assigned on page 362, be regarded as cyanate of ammonia; that compound, in fact, exhibiting totally different chemical relations.

Decompositions. Urea is decomposed by *dry distillation* somewhat above its melting point, and is resolved for the most part into ammoniacal gas and a residue of cyanuric acid. If the heat be continued, the decomposition-products of that acid make their appearance (Wöhler):

$$3C^2H^4N^2O^2 = 3NH^3 + C^6H^3N^3O^6.$$

Urea when fused gives off pure ammoniacal gas, and becomes continually more turbid, viscid, and pasty, yielding white granules of cyanuric acid, till finally the evolution of ammonia ceases, and the residue solidifies to a dirty white, pulverulent mass of cyanuric acid. The residue dissolves in a considerable quantity of boiling water (with the exception of a small quantity of dirty white matter accidentally present), and the solution yields nothing but crystals of cyanuric acid. If the heat be discontinued before the ammonia is entirely driven off, the residue consists entirely of cyanurate of ammonia, with a small quantity of still undecomposed urea. If the heat be continued after the evolution of ammonia has ceased, the cyanuric acid volatilizes in the form of cyanic acid. As the vapour of this acid still meets with ammonia in the apparatus, it unites with that substance, and condenses in the form of a white sublimate of cyanate of ammonia, which, when dissolved in water and evaporated again, yields urea (p. 362), and when treated with hydrochloric acid, yields, in addition to cyanic acid, carbonic acid resulting from the decomposition of the former. This circumstance formerly led to the erroneous opinion that the sublimate consists of carbonate of ammonia. The sublimate does not contain hydrocyanic acid. That portion of the cyanic acid which finds no ammonia to combine with, appears in the form of a liquid distillate, which soon solidifies as insoluble cyanuric acid. (Liebig & Wöhler.)—When perfectly pure urea is distilled, it gives off, under certain circumstances, a very large quantity of water, together with carbonic acid and carbonate of ammonia; and the residue consists, not of cyanuric acid, but of the compound $C^6N^4H^4O^4$. (Liebig & Wöhler, *Ann. Pharm.* 54, 371; 57, 114; 58, 255.) According to Liebig & Wöhler, this decomposition takes place during slow distillation; according to a later observation of Liebig's, on the contrary, it takes place only when the distillation is conducted as quickly as possible. In this case, the urea is said to be wholly resolved into water, carbonic acid, and $C^6N^4H^4O^4$; such decomposition, however, cannot be expressed by an equation; the real decomposition appears to be that which is represented in the following equation given by Gerhardt (*N. J. Pharm.* 8, 388):

$$4C^2N^2H^4O^2 = 2CO^2 + 4NH^3 + C^6N^4H^4O^4.$$

Urea gradually heated in a retort, melts, becomes viscid, yields a sublimate of carbonate of ammonia, and leaves a dry opaque mass, which volatilizes when further heated, sublimating in the form of a white crust with yellow spots. This second sublimate is tasteless, and dissolves very sparingly in hot water, forming a solution which reddens litmus, and on cooling deposits crystalline grains resembling uric acid. (Fourcroy & Vauquelin.) — According to Prout, a portion of the urea sublimes undecomposed. According to Proust, the urea first gives off water, then a large quantity of carbonate of ammonia, and lastly a small quantity of oil, leaving behind a trace of carbon; hydrocyanic acid did not appear to be given off.—2. *In the open fire*, urea volatilizes without residue, giving off an odour of ammonia. (Fourcroy & Vauquelin.)—When *chlorine* is passed through the aqueous solution of urea, carbonic acid and nitrogen are evolved. The residue when distilled yields aqueous hydrochloric acid; afterwards, when it has become dry, a sublimate of carbonate and hydrochlorate of ammonia together with benzoic acid; but urea is not completely decomposed by chlorine. (Fourcroy & Vauquelin.) ¶ According to Wurtz (*Compt. rend.* 24, 436; *Ann. Pharm.* 64, 307) dry chlorine gas passed through melted urea, forms cyanuric acid, sal-ammoniac, hydrochloric acid, and nitrogen. ¶—4. *Nitrous acid*, as well as nitric acid, which is coloured by nitrous or hyponitric acid, decomposes urea completely at ordinary temperatures, yielding water, nitrogen, and carbonic acid gas (Millon, *N. Ann. Chim. Phys.* 8, 233; also *J. pr. Chem.* 30, 370):

$$C^2H^4N^2O^2 + 2NO^3 = 4HO + 2CO^2 + 4N.$$

(Compare, however, Liebig & Wöhler, *Ann. Pharm.* 26, 261.)

¶ Urea is likewise resolved into carbonic acid and nitrogen by the action of a solution of mercurous nitrite in nitric acid; and if the carbonic acid be received in Liebig's potash-apparatus, the quantity of urea may be very exactly determined, being equal to that of the carbonic acid multiplied by 1·371. (Millon, *Compt. rend.* 26, 119.) ¶—5. Colourless *nitric acid* does not decompose urea at ordinary temperatures. (Millon.) Even when it is added in excess to the urea, and evaporated at a temperature between 60° and 80°, undecomposed nitrate of urea remains mixed with a very small quantity of nitrate of ammonia. (Heintz.) Fuming nitric acid decomposes urea with strong effervescence, yielding nitrogen, nitrous gas, carbonic acid, and nitrate of ammonia. Dilute nitric acid slowly and continuously heated in a distillatory apparatus with (impure) urea, gives off, with slight effervescence, nitrogen, nitrous gas, carbonic acid, hydrocyanic acid, and an oil, till, after two days, the residue becomes thick, and explodes with violence. (Fourcroy & Vauquelin.)—6. Urea boiled with excess of *oil of vitriol* is completely resolved into carbonic acid gas and sulphate of ammonia (Dumas):

$$C^2H^4N^2O^2 + 2HO = 2CO^2 + 2NH^3.$$

The water required for this decomposition is supplied by the oil of vitriol. [In all such decompositions of urea, when 2HO is added, 100 parts of urea must yield 73·33 carbonic acid and 56·67 ammonia, together = 130 pts.]—10 grammes of urea decomposed in this manner yield 373¼ cub. cent. of carbonic acid gas at 0°, and under a pressure of 0·76 met., corresponding to 19·9 per cent. of carbon. (Dumas.)—On this relation are founded the methods of determining the quantity of urea in urine proposed by Heintz (*Pogg.* 66, 114; 68, 393) and Ragsky. (*Ann.*

Pharm. 56, 39.) With attention to certain precautions, the proportion of urea may be very exactly estimated by boiling the urine with oil of vitriol, and ascertaining either the quantity of carbonic acid evolved, or the quantity of ammonia precipitated in the form of chloroplatinate of ammonium.—With anhydrous sulphuric acid, urea evolves a considerable degree of heat, and yields a compound which dissolves in water with great rise of temperature, forming a solution from which, after a while, sulphate of ammonia separates. (Liebig & Wöhler.)—Urea in the state of very dilute solution is not decomposed by sulphuric acid, phosphoric acid, or monophosphate of soda. (Lehmann, *J. pr. Chem.* 25, 5, & 7.)—Strong hydrochloric acid does not decompose urea in the cold, and but very slowly at a boiling heat, a small quantity of sal-ammoniac being then produced. (Heintz.)—7. Urea heated with *hydrate of potash* is almost wholly resolved into ammonia and carbonate of potash. (Dumas.)—Common hydrate of potash containing more than 1 At. water gives off less ammonia; but if it be freed from excess of water by ignition, mixed with 0·3 grm. of urea, and gradually heated to commencing redness, the neck of the retort being filled with lumps of hydrate of potash and made to dip under mercury, 214·8 cub. cent. of ammonia are evolved, corresponding to 45·3 per cent. of the nitrogen in the urea. (Dumas.)—8. Urea dissolved in *water* is not decomposed by continued boiling, and therefore gives off no ammonia (Wöhler); but when heated with a small quantity of water somewhat above 100°, it is converted into carbonate of ammonia. (Pelouze.)—¶ At 120° the transformation is slow, but between 220° and 240° it is completed in 3 or 4 hours. When an aqueous solution of urea is mixed with an ammoniacal solution of chloride of barium, and heated in a closed tube to the temperature just mentioned, a quantity of carbonate of baryta is obtained, bearing a fixed relation to the quantity of urea in the liquid, and serving therefore to determine that quantity. (Bunsen, *Ann. Pharm.* 65, 375; *N. J. Pharm.* 16, 151; *Pharm. Centr.* 1848, 417; *Jahresber.* 1847-8, 989.) According to Wittstein (*Repert. Pharm.* [3], 6, 207,) pure urea is gradually decomposed, with formation of carbonate of ammonia, when its aqueous solution is boiled in open vessels; hence, to avoid loss, Wittstein recommends that the solution be evaporated below the boiling point.—Boussingault, on the contrary, found (*N. Ann. Chim. Phys.* 29, 472) that a solution of 1 pt. urea in 100 water gave off scarcely a trace of ammonia, when boiled down to half its bulk (care being taken not to heat the glass and the urea adhering to it to a higher temperature). When the liquid was reduced to ¼ of its original volume, ammonia began to go off, but only because the liquid had then become so thick that portions of it were heated above 100°. When a solution of 1 pt. urea in 100 pts. water was boiled with magnesia or lime, ammonia was given off; but when a similar solution was continuously heated with lime to 40°, and air passed through, or when a solution of urea mixed with lime or carbonate of soda was evaporated in vacuo, at a temperature between 45 and 50°, no perceptible quantity of ammonia was formed. ¶—The aqueous solution remains unaltered for months. (Prout.)—Urea dissolved in 100 parts of water and set aside for some months in a well-closed bottle, is converted very slowly and but partially, and without evolution of gas or formation of any other substance, into carbonate of ammonia. (Vauquelin.)—If glue, white of egg, mucus, or any similar substance, be added to the solution of urea, the transformation into carbonate of ammonia takes place rapidly. (Fourcroy & Vauquelin.)—The statement of these chemists that

acetate of ammonia is likewise produced, has not been confirmed. Hence also arises the ammoniacal putrefaction of human urine, inasmuch as that liquid, in addition to urea, contains mucus, and sometimes also albumen. (Comp. *Putrefaction of Urine*, p. 107.)—Common sugar or milk sugar added to human urine stops its putrefaction for months. (Liebig, *Ann. Pharm.* 50, 173.)—9. Urea mixed with an aqueous solution of *nitrate of silver*, and evaporated to dryness, is completely resolved into nitrate of ammonia and prisms of cyanate of silver. (Liebig & Wöhler, *Ann. Pharm.* 26, 301):

$$C^2H^4N^2O^2 + AgO,NO^5 = NH^3,HO,NO^5 + C^2NAgO^2.$$

Urea evaporated with an aqueous solution of *sugar of lead*, yields ammonia and a precipitate of carbonate of lead in shining scales. (Liebig & Wöhler, *Ann. Pharm.* 26, 301.)

Compounds. A. With *Water.* Urea dissolves quickly in water, with lowering of temperature; it requires for solution less than 1 pt. of water at 15°, and dissolves in all proportions at 100°. (Prout.)—The concentrated solution has the consistence of syrup. According to earlier statements, urea deliquesces in moist air; according to Pelouze, it does not; but when triturated with Glauber's salt and other salts rich in water of crystallization, it abstracts their water and forms a solution therewith.

B. With *Acids.* Only the stronger acids are capable of combining with urea. (Pelouze.) All the compounds so formed are acid. The urea may be recovered from them by digesting them with a fixed alkaline carbonate and exhausting with alcohol.

a. With *Sulphuric acid.* A mixture of 100 pts. oxalate of urea, 125 crystallized gypsum, and a small quantity of water, is slightly warmed, the mixture exhausted with 4 times its weight of alcohol, and the filtrate evaporated.—Granular crystals or needles, having a fresh, pungent taste. (Cap & Henry.)

b. With *Hydrochloric acid.* Urea absorbs hydrochloric acid gas. (Pelouze, Hagen.) If it be saturated with that gas, at first in the cold, but ultimately at 100°, and the pale yellow oil thus formed be freed by a current of air from the excess of hydrochloric acid, the oil solidifies on cooling in the form of a white, hard, laminar, radiated mass, the solidification being attended with development of heat. The solidified mass deliquesces rapidly in the air, forming a very acid liquid, which exhales vapours of hydrochloric acid; when dissolved in water, it is immediately decomposed into free hydrochloric acid and free urea. In boiling absolute alcohol, it appears to dissolve without alteration; but as the solution cools, a very small quantity of sal-ammoniac crystallizes out of it, having probably been formed during the absorption of the hydrochloric acid gas. Nitric acid added to the alcoholic solution immediately throws down nitrate of urea. (Erdmann & Krutzsch, *J. pr. Chem.* 25, 506.) ¶ Hydrochlorate of urea heated to 145°, is resolved into sal-ammoniac and pure cyanuric acid; at 320°, the compound $C^6N^4H^4O^4$, discovered by Liebig & Wöhler as a product of the decomposition of urea, is produced. (De Vry, *Ann. Pharm.* 61, 242.) ¶.

				Erdmann & Krutzsch.
$C^4H^4N^2O^2$	60·0	62·24	.....	62·65
HCl	36·4	37·76	.....	37·35
$C^2Ad^2O^2 + HCl$	96·4	100·00	.....	100·00

Pelouze found the same composition.—Cap and Henry prepare this compound by decomposing oxalate of urea with an alcoholic solution of chloride of calcium, and evaporating the filtrate to the crystallizing point.

c. With *Nitric acid.* First obtained by Fourcroy and Vauquelin.—From a cold aqueous solution of urea, not too dilute, nitric acid throws down, either immediately or after a while, a precipitate of nitrate of urea in white crystalline scales, the precipitation being attended with slight evolution of heat.—If the nitric acid contains nitrous acid, a disengagement of gas takes place, arising from partial decomposition. The colder and more concentrated the urea-solution and the acid may be, the more quickly and completely is the urea precipitated, so that the mixture becomes nearly solid. But even when 1 pt. of the solution is mixed with 2 pts. of colourless nitric acid of specific gravity 1·3, the liquid retains from 8 to 10 parts of urea, because nitrate of urea is somewhat soluble, even in concentrated nitric acid. (Heintz, *Pogg.* 60, 144.)

When 1 measure of nitric acid, of sp. gr. 1·322, is added to 1 measure of an aqueous solution of urea of various degrees of concentration, the following effects are produced:—1 pt. urea to 10·6 pts. water: immediate precipitation of scales;—1 urea to 15 water: gradual formation of scales;—1 urea to 20·4 water: the scales begin to form after 40 minutes, and increase at 8°;—1 urea to 24 water: after a few hours, a large quantity of crystals are produced (if the volume of nitric acid used is less than that of the urea, the crystals do not appear till the solution is cooled to 0°);—1 urea to 25·4 water at 13°: after a few hours, a large quantity of radiated crystalline laminæ, which increase on further addition of acid;—1 urea to 29·1 water at 13°: after a few hours, an extremely small quantity of scales, which increase on cooling, or on further addition of acid;—1 urea to 29 water at 9°: in one hour a tolerably large quantity of crystals, likewise increasing at 0°, or on the addition of acid;—1 urea to 71·2 water with 2 volumes of nitric acid at 0°: in a cylinder, nothing in 3 days, but in a watch-glass, scales at the edge of the liquid in 24 hours;—1 urea to 100 water with 1 vol. nitric acid in the watch-glass: a slight appearance of efflorescence in 3 days, after the evaporation of ¼ of the mixture. (Lehmann, *J. pr. Chem.* 25, 10.)

Nitrate of urea precipitated from coloured urea is likewise brownish or yellowish; to obtain it colourless, recourse must be had to the methods of Wöhler, Cap & Henry, and Millon (p. 364).

Colourless, transparent, shining scales, tables, and prisms, which redden litmus strongly.

	Crystallized.		Regnault.		Heintz.		Fehling.
2 C	12	9·75	10·04	10·01	9·82	9·9
5 H	5	4·07	4·09	4·11	4·12	4·3
3 N	42	34·15	34·16	34·34	34·57	
3 O	64	52·03	51·71	51·54	51·49	
C^2AdO^2,HO,NO^5	123	100·00	100·00	100·00	100·00	

		Fehling.	Marchand.	Prout.	Lecanu.	Lehmann.
$C^2H^4N^2O^2$	60	48·78	....	52·63	53·5	52·93
NO^5	54	43·90	43·8 43·73	47·37	46·5	47·00
HO	9	7·32				
	123	100·00		100·00	100·0	99·93

The crystals do not give off water at 110° (Regnault, *Ann. Pharm.* 26,

39).—The crystals examined by Heintz, (*Pogg.* 66, 118,) were obtained from very acid liquids, and were dried at 110°; those of the first analysis were produced from the urea of urine, those of the second from artificial urea (prepared by Liebig's process, p. 365). The crystals have the same composition, whether they are recrystallized from the solution in water or in nitric acid. (Fehling, *Ann. Pharm.* 55, 249.)

Prout, Lecanu, and Lehmann, (*J. Pharm.* 17, 651,) overlooked the 1 At. HO in the compound. Marchand, in fact, assumes the existence of the anhydrous compound, believing that he obtained it under peculiar circumstances not accurately known; but as Heintz and others could not obtain this compound in any way whatever, its existence may be regarded as doubtful. Moreover, Marchand once obtained crystals containing 61·13 per cent. nitric acid = $C^2H^4N^2O^2$,HO,2NO^5. When they were heated to 140°, the proportion of acid rose to 65·72 per cent., which Marchand attributed to loss of water; the aqueous solution of this binitrate of urea, mixed with urea, yielded crystals, containing 55 per cent. of nitric acid, therefore=$2C^2H^4N^2O^2$,HO,3NO^5; and it was only when the mother-liquor of these crystals was evaporated with a still larger quantity of urea, that the ordinary crystals, containing 44·1 per cent. of acid, were produced.

The crystals when continuously heated to 100°, diminish in weight by gradual decomposition; after several days, the decrease amounts to 12 per cent., and the residue, which is then in the fused state, distinctly gives off gas-bubbles. This decomposition takes place more rapidly at 120°, carbonic acid being then given off, at first mixed with $\frac{1}{3}$ to $\frac{1}{2}$ its volume of nitrogen, but afterwards in a state of purity; no nitric oxide is observed to go off. Nitrate of urea, which has lost 7 per cent. in weight by being thus heated, retains only 37 to 40 per cent. of nitric acid. (Fehling.) At 120°, nitrate of urea diminishes continually in weight, and when it no longer exhibits any decrease in weight at that temperature, it retains only 35·66 per cent. of nitric acid. (Heintz.) Though nitrate of urea gives off gas-bubbles but slowly at 130°, it quickly gives off the whole of its gas at that temperature, if mixed with spongy platinum; if the residue be then heated to a temperature between 170° and 230°, it yields, in presence of spongy platinum, peculiar products different from those which it would yield alone. (Reiset & Millon, *N. Ann. Chim. Phys.* 8, 288.) At 14°, nitrate of urea gives off carbonic acid gas and nitrous oxide, almost exactly in the proportion by volume of 2 : 1, and leaves a deliquescent mixture of urea and nitrate of ammonia:

$$4(C^2H^4N^2O^2,HO,NO^5) = 4CO^2 + 2NO + 2C^2H^4N^2O^2 + 3(NH^3,HO,NO^5.)$$

On further heating this residue, the nitrate of ammonia is resolved into nitrous oxide and water, and the urea [with addition of water and nitrate of ammonia] into ammonia and carbonic acid, so that nothing remains behind (Pelouze):

$$2(C^2H^4N^2O^2) + 3(NH^3,HO,NO^5) = 6NO + 8HO + 4NH^3 + 4CO^2.$$

The residue left after the heat has been raised to 140°, contains a trace of a peculiar acid, which crystallizes from the solution of the residue in boiling water, in small greyish white, shining laminæ, whilst the urea and the nitrate of ammonia remain in solution. This acid has but a faint taste, but reddens litmus distinctly. When subjected to dry distillation, it yields acid products, and leaves no residue. With potash it yields

ammonia only when heated, and then very slowly. Its aqueous solution forms an abundant white precipitate with subacetate of lead, and with nitrate of silver. Its formula appears to be $C^2H^3N^2O^4$. (Pelouze.) [If this acid were composed of $C^2H^4N^2O^4 = C^2Ad^2,O^4$, it would be a monobasic acid of the nucleus C^2Ad^2, of which urea is the aldide.] Nitrate of urea sprinkled on a red-hot spoon, boils up and exhibits a small transient flame.

Nitrate of urea gives up its acid to caustic alkalis and their carbonates. It dissolves sparingly in water, very sparingly in nitric acid, especially if concentrated, and sparingly also in alcohol.

Urea likewise forms definite, sparingly soluble, crystalline compounds with oxalic and tartaric acid. (*q. v.*) The statement of Cap & Henry, that urea is also capable of uniting with the weaker organic acids, such as lactic, hippuric, and uric acid, is not confirmed by the experiments of Lecanu & Pelouze.

C. With *Metallic Chlorides and Oxygen-salts.*—The affinity of urea for these compounds being but small, it forms crystalline compounds with those only which are about as soluble as itself in water and alcohol. (Werther.)

a. With *Chloride of Sodium.* A mixture of the cold saturated solutions of urea and common salt in equal numbers of atoms, yields, on evaporation, shining oblique rhombic prisms. The form of these crystals is nearly that of *fig.* 85, together with the face below i; $u' : u = 139°$; $u' : t = 110° 30'$; $a : a$ above $i = 146°$; $a : t = 107°$; $f : u = 126°$. The compound melts between 60° and 70°, gives off 12·55 per cent. of water of crystallization at 100°, and at a higher temperature evolves ammoniacal vapours, and leaves 42·64 per cent. of common salt. The crystals deliquesce in the air. The aqueous solution, even if the compound has been heated till it fuses, and the solution itself raised to the boiling point, still yields the same crystals. Nitric acid added to a concentrated solution throws down the greater part of the urea; but a solution only moderately concentrated is not precipitated, even by a large quantity of nitric acid, or by 12 times its volume of alcohol. Hence urea is but very imperfectly precipitated by nitric acid, from a solution containing common salt, *e. g.*, from evaporated urine. Oxalic acid added to the solution throws down, after some time, crystals of [acid] oxalate of soda, whereupon the mother-liquor deposits on evaporation laminæ of oxalate of urea. Absolute alcohol partially decomposes the crystals, dissolving out all the urea, with but little of the common salt. (Werther.)

	Crystallized.				Werther.
$C^2H^4N^2O^2$	60·0	....	43·92		
NaCl	58·6	....	42·90	.....	42·64
2Aq.	18·0	....	13·18	.....	12·55
$C^2H^4N^2O$,NaCl + 2Aq.	136·6	....	100·00		

Sal-ammoniac crystallizes from an aqueous solution containing urea in cubes instead of octohedrons, and common salt in octohedrons or cubo-octohedrons, instead of cubes; these crystals, however, appear to contain but very little urea.

b. With *Nitrate of Soda.* A mixture of very concentrated solutions of the two substances, in equal numbers of atoms, yields, on cooling, long prisms, which, in a dry atmosphere, soon become dull from loss of

a portion of their water. They begin to melt at 35°, but do not liquefy completely even at 100°; at 120°, they give off all their water; at 142°, the compound suffers further decomposition, and, when suddenly heated, explodes with violence. Even after being fused, redissolved in water, and boiled, it still crystallizes in the same form. If it has been heated sufficiently to drive off its water, and then dissolved in water, the solution yields by very slow evaporation, first nitrate of soda, then urea; but if this mixture of crystals be redissolved in a small quantity of hot water, the compound, on cooling, recrystallizes as a whole. The decomposition which ensues on slow evaporation, is probably due to the different solubilities of the constituents. The aqueous solution is not precipitated even by a very large excess of nitric or oxalic acid, not even by nitrate of silver. (Werther.)

	Crystallized.			Werther.
$C^2H^4N^2O^2$	60·0	36·76		
NaO,NO^5	85·2	52·21		50·27
2Aq.	18·0	11·03		10·42
$C^2H^4N^2O^2 + NaO,NO^5 + 2Aq.$	163·2	100·00		

Sal-ammoniac, chloride of potassium, chloride of barium, nitre, nitrate of baryta, and nitrate of strontia crystallize in the free state from a solution containing urea.

c. With *Nitrate of Lime.* $C^2H^4N^2O^2 + CaO,NO^5$. The aqueous, or better, the alcoholic solution of the two substances yields, when evaporated over oil of vitriol, deliquescent prisms having a vitreous lustre. At 100°, they give off only 0·94 per cent. of hygroscopic water, and nothing more till they are heated to 140°; at 145° they begin to fuse, giving off first ammoniacal and then acid vapours; but the decomposition is not complete even at 180°. When suddenly heated, they detonate violently, leaving a residue of carbonate of lime. The lime in the compound amounts to 10·5 per cent. The aqueous solution is not precipitated, either by nitric acid or by potash free from carbonic acid, but oxalic acid throws down oxalate of lime and oxalate of urea. (Werther.)

d. With *Nitrate of Magnesia.* $C^2H^4N^2O^2 + 2\,(MgO,NO^5)$. The solution of the two substances in absolute alcohol yields, when evaporated in vacuo, large, shining, oblique rhombic prisms. *Fig.* 84, the *a*-faces meeting above, the edges between *u* and *i* replaced by planes; $u' : u = 135°$; $a : a = 140°$; $u : i = 128°\ 42'$; $u : f = 126°\ 30'$; $i : f$ backwards $= 97°\ 20'$. The crystals fuse at 85°, giving off 1·9 per cent. of water, probably merely hygroscopic, and forming an opaque fluid, which does not solidify till some time after cooling. At a higher temperature, the compound decomposes like that with nitrate of lime, and leaves 10·42 per cent. of magnesia. The fused mass dissolved in absolute alcohol, yields the original crystals again. The compound is deliquescent; in the state of aqueous or alcoholic solution, it is not decomposed by long boiling. Nitric acid throws down only part of the urea, even from a concentrated solution; oxalic acid, potash free from carbonic acid, and nitrate of silver, produce no precipitate. (Werther.)

e. With *Protochloride of Mercury.* This compound cannot be obtained in the crystalline form from the aqueous solution, but separates in that form from a solution of the two substances in boiling absolute

alcohol. Flat prisms with curved faces, and having a faint pearly lustre. At 125° they begin to melt without losing water, fuse completely at 128°, and at 130°, solidify in the form of a white paste, from which absolute alcohol extracts corrosive sublimate and a trace of sal-ammoniac. Boiling water extracts small quantities of these two substances, and leaves a yellow powder which, when heated, gives off ammoniacal vapours without fusing, assumes a transient red colour, and yields a sublimate of calomel mixed with mercury. The undecomposed crystals dissolve sparingly in cold water, and are decomposed by boiling water; the cold solution evaporated without the application of heat, yields crystals, first of corrosive sublimate, then of the compound, and then of urea. In absolute alcohol the compound is more soluble, especially at a boiling heat; but even this solution undergoes partial decomposition, when it evaporates at ordinary temperatures. This solution is not precipitated by nitric or oxalic acid, but gives a yellow precipitate with potash. (Werther.) The compound yields with potash a white precipitate, resembling amide of mercury, and, like that compound, exploding when heated. (Piria, *Compt. rend.* 21, 686.)

	Crystallized.				Werther.
$C^2H^4N^2O^2$	60·0	....	18·14		
2 Hg	200·0	....	60·46	.....	60·38
2 Cl	70·8	....	21·40	.....	20·94
$C^2H^4N^2O^2,2HgCl$	330·8	....	100·00		

¶ *f.* With *Mercuric Nitrate.* $C^2H^4N^2O^2,4HgO,NO^5$. Precipitated in the form of a snow-white, almost insoluble compound, when any liquid containing urea is mixed with a solution of mercuric nitrate containing no free acid. This reaction is said to afford, with certain precautions, a ready method of estimating the quantity of urea in urine. As nitric acid is set free in the process, and as this free acid prevents the further action of the nitrate, it is necessary to neutralize the liquor with baryta-water, after each addition of the nitrate. (Liebig, *Chem. Soc. Qu. J.* 5, 30.) ¶

g. With *Nitrate of Silver.*—*a.* $C^2H^4N^2O^2 + AgO,NO^5$. Concentrated aqueous solutions of the two substances mixed together, either cold or at 50°, immediately yield large crystals, into which also the rest of the liquid, when evaporated at 50° in vacuo over oil of vitriol, is converted to the last drop. Large, shining, oblique, rhombic prisms. *Fig.* 85, without the *f*-face, but with truncation of the lateral edges between *u* and *t*; $u' : u = 118°$; $i : u'$ or $u = 110°$; $i : a = 160°$; $a : a = 140°$; $a : t = 110°$. The dry crystals, when heated, give off a trace of hygroscopic water, fuse, yield ammonia, and then nitrous vapours; when suddenly heated, they exhibit fiery detonation accompanied with red vapours, and leave metallic silver. When the pulverized compound has been heated for 18 hours in the water-bath, a small part of it is resolved into cyanate of silver and nitrate of ammonia, the powder at the same time cohering together in a mass which becomes moist. The dilute aqueous solution becomes turbid by continued boiling, and on cooling, deposits long prisms of cyanate of silver (*comp.* p. 369). But the supernatant liquid still contains a large quantity of the undecomposed compound, and even after very long boiling, the conversion of the silver-oxide into cyanate is not complete. The crystals dissolve without

decomposition in considerable quantities of water, either hot or cold, or of alcohol. Nitric acid added to these solutions throws down part of the urea; oxalic acid produces an immediate precipitate of oxalate of silver; alcoholic soda-solution forms, with the aqueous solution of the compound, a yellowish precipitate, which blackens when boiled with water, contains 83·94 per cent. of silver-oxide, and is therefore, perhaps, a compound or mixture of 5 At. silver-oxide with 2 At. urea [or 3 At. silver-oxide with 1 At. urea.] (Werther.)

β. $C^2Ad^2,O^2+2(AgO,NO^5)$. The aqueous solution of 1 At. urea, mixed with a solution of 3 or 4 At. nitrate of silver, yields, when evaporated in vacuo, first crystals of the compound *α*, then of the compound *β*, and ultimately of pure nitrate of silver. The crystals of *β* are large, shining, right rhombic prisms. Their form is nearly that of *Fig.* 73, but without *y*-faces, and with the *p*-face; $p : a = 127°$; $p : i = 143° 36'$; $ú : u = 112° 30'$. The crystals contain no water. The chemical relations resemble those of *α*. (Werther.)

Crystals α.				Werther.
$C^2Ad^2O^2$	60	....	26·09	
AgO	116	....	50·43	..... 49·63
NO^5	54	....	23·48	
$C^2Ad^2O^2,AgO,NO^5$	230	....	100·00	

Crystals β.				Werther.
$C^2Ad^2O^2$	60	....	15	
2 AgO	232	....	58	..... 83·34
2 NO^5	108	....	27	
$C^2Ad^2O^2,2(AgO,NO^5)$	400	....	100	

D. With *Metallic Oxides.* Urea does not precipitate any metallic oxide from its acid solution; but when it is added together with an alkali, a compound of the metallic oxide with urea is often precipitated. The compound with silver-oxide is grey, and detonates when heated, the silver being reduced. (Prout, *comp.* Werther, also Liebig, p. 374.)

E. Urea dissolves in 5 pts. of cold alcohol of sp. gr. 0·816, and in less than 1 pt. of boiling alcohol, from which it crystallizes on cooling. (Prout.) It is very sparingly soluble in ether; but according to Hünefeld (*J. pr. Chem.* 7, 43), it dissolves readily in a mixture of ether and alcohol; hence ether does not precipitate it from the alcoholic solution. This is, perhaps, the origin of the statement made by O. Henry, that urea is easily soluble in ether. Urea does not dissolve in oil of turpentine. (Pfaff, Prout.) ¶ From a solution containing urea and ferrocyanide of potassium, the latter separates, in successive crystallizations, accompanied by very variable quantities of urea (the quantity has been found to reach as high as 41 per cent.); the product is, however, a mere mixture, not a definite compound. (Hunaut, *N. J. Pharm.* 18, 411.) ¶

Copulated Compounds.

¶ **Methyl-urea.** $C^4H^6N^2O^2 = C^2H^2,C^2H^4N^2O^2 = C^2\left\{\begin{matrix}H^2\\C^2H^3\end{matrix}\right\}N^2O^2$.

WURTZ. *Compt. rend.* 32, 414; *Ann. Pharm.* 80, 346; *J. pr. Chem.* 53, 44; *Pharm. Centr.* 1851, 487; *Jahresber.* 1850, 384; see also Memoirs cited at the head of *Methylamine*, p. 313.

Acetyl-urea, Methyl-Harnstoff, Acetyl-Harnstoff.

Formation and Preparation. By a transformation of cyanate of methylamine analagous to the conversion of cyanate of ammonia into common urea (p. 365.) 1. Cyanate of methyl dissolves in aqueous ammonia, with evolution of heat, and the solution, when evaporated, yields crystals of methyl-urea. (Wurtz, *Ann. Pharm.* 71, 328):

$$C^2H^3O,C^2NO + NH^3 = C^4H^6N^2O^2.$$

2. When solutions of sulphate of methylamine and cyanate of potash are mixed and evaporated at a gentle heat, and the residue treated with alcohol, a solution is obtained which likewise yields crystals of methyl-urea on evaporation. (Wurtz, *N. Ann. Chim. Phys.* 30, 460.)

Properties. Long transparent four-sided prisms, which deliquesce on exposure to the air. The aqueous solution is neutral.

	Calculation.		
4 C	24	.....	32·43
6 H	6	.....	8·11
2 N	28	.....	37·84
2 O	16	.....	21·62
$C^2\left\{\begin{matrix}H^3\\C^2H^3\end{matrix}\right\}N^2O^2$	74	.....	100·00

Nitrate. $C^4H^6N^2O^2,HO,NO^5$. Precipitated on adding nitric acid to a somewhat concentrated aqueous solution of methyl-urea. Much less soluble than the base itself.

¶ **Dimethyl-urea.** $C^6H^8N^2O^2 = (C^2H^2)^2,C^2H^4N^2O^2 = C^2\left\{\begin{matrix}H^2\\(C^2H^3)^2\end{matrix}\right\}N^2O^2$.

WURTZ. *Vid. Memoirs cited on page 376.*

This compound is obtained—1. By the action of water on cyanate of methyl. (*Ann. Pharm.* 71, 328):

$$2(C^2H^3O,C^2NO) + 2HO = 2CO^2 + C^6H^8N^2O^2.$$

2. By the action of methylamine on cyanate of methyl. (*Ann. Pharm.* 80, 348):

$$C^2H^3O,C^2NO + C^2H^5N = C^6H^8N^2O^2.$$

Crystallizes readily; fuses at about 97°; is permanent in the air; may be volatilized without decomposition; and dissolves readily in water and alcohol.

	Calculation.		
6 C	36	.....	40·91
8 H	8	.....	9·09
2 N	28	.....	31·82
2 O	16	.....	18·18
$C^2\left\{\begin{matrix}H^2\\(C^2H^3)^2\end{matrix}\right\}N^2O^2$	88	.....	100·00

By the action of potash, it is resolved into carbonic acid and methylamine:

$$C^6H^8N^2O^2 + 2KO + 2HO = 2(KO,CO^2) + 2C^2H^5N.$$

With nitric acid, it forms a salt composed of $C^6H^6N^2O^2,HO,NO^5$. ¶

Ureo-carbonic Acid. $C^4N^2H^4O^6 = C^2Ad^2O^2,2CO^2$.

Liebig. (1846.) *Ann. Pharm.* 58, 260.

The crystallized compound ether, which is abundantly deposited, together with urethylane, on passing cyanic acid vapour into alcohol or ether, contains the constituents of vinic ether and of hypothetically anhydrous ureo-carbonic acid; so that its formula is $C^4H^5O,C^4N^2H^3O^5$. When treated with baryta-water or alcoholic potash, it is resolved into alcohol and a ureo-carbonate of the alkali. These salts are resolved by the slightest heat into urea, carbonic acid, and an alkaline carbonate. (Liebig):

$$C^4N^2H^4O^6 = C^2N^2H^4O^2 + 2CO^2.$$

Ureo-carbonate of Methyl. $C^2H^3O,C^4N^2H^3O^5$.

Richardson. (1837.) *Ann. Pharm.* 23, 138.

When cyanic acid vapour evolved from heated cyanuric acid is passed into pure wood-spirit, a large quantity of colourless crystals of this compound is quickly formed; they must be repeatedly washed with water, and then dried at 100°. When heated, they volatilize partly undecomposed, partly resolved into methylene, ammonia [and carbonic acid ?] and cyanuric acid, which remains behind. [Probably thus:

$$3(C^2H^3O,C^4N^2H^3O^5) = C^6N^3H^3O^6 + 3C^2H^2 + 3NH^3 + 6CO^2.]$$

The crystals heated with potash are decomposed in a similar manner to the corresponding ethyl-compound. They dissolve readily in water, wood-spirit, and alcohol, more abundantly, however, with the aid of heat. The solutions do not redden litmus. (Richardson.)

				Richardson.
6 C	36	....	30·51	..... 30·64
2 N	28	....	23·72	..... 23·65
6 H	6	....	5·09	..... 5·11
6 O	48	....	40·68	..... 40·60
	118	....	100·00	..... 100·00

i. Secondary Nucleus. C^2NH.

Cyanogen, C^2N, and Hydrocyanic Acid, C^2NH.

Literature for Cyanogen, Hydrocyanic Acid, and Metallic Cyanides.

SCHEELE. *Opusc.* 2, 148.
BERTHOLLET, *Mém. de l'Acad. de Sc. à Paris*, 1787, 148; also *Crell. Ann.* 1795, 1, 70.
RICHTER. *N. Gegenst. der Chemie*, 11, 49.
BUCHOLZ. *A. Gehl.* 1, 406.
PROUST. Hydrocyanic acid. *Ann. Chim.* 60, 185 and 225; also *N. Gehl.* 3, 549.
F. v. ITTNER. *Beiträge zur Gechichte der Blausäure.* Freiburg and Constanz, 1809.
GAY-LUSSAC. *Ann. Chim.* 77, 128; also *Schw.* 2, 204; also *Gilb.* 40, 229.—*Ann. Chim.* 95, 136; also *Schw.* 16, 1; also *Gilb.* 53, 1 and 138.
H. DAVY. *Gilb.* 54, 383.
VAUQUELIN. *Ann. Chim. Phys.* 9, 113; also *Schw.* 25, 50.—*Ann. Chim. Phys.* 22, 132; also *N. Tr.* 9, 1, 124.
WÖHLER. *Pogg.* 3, 177.
JOHNSTON. *N. Ed. Phil. J.* 1, 75; also *Schw.* 56, 341.
PORRETT. Cyanides. *Phil. Trans.* 1814, 527; also *Schw.* 17, 258; also *Gilb.* 53, 184; also *N. Tr.* 3, 2, 422.
RAMMELSBERG. Cyanides. *Pogg.* 38, 364; 42, 111.
FERD. & EDW. ROGERS. *Phil. Mag. J.* 4, 91.

History. Prussian blue was accidentally discovered in 1704 by Diesbach & Dippel, in Berlin. Macquer found that this substance by treatment with lime-water was resolved into calx of iron (ferric oxide) and a combustible colouring matter, which when combined with potash converted the latter into *phlogisticated* potash (ferrocyanide of potassium). Scheele, in 1782, succeeded in preparing *Prussic* or *Hydocyanic acid* in the state of aqueous solution from these compounds, and in distinguishing their constituent elements, which he stated to be ammonia, *acid of air*, and phlogiston. (Ammonia is nitrogen and hydrogen; acid of air or carbonic acid + phlogiston, according to the phlogistic theory then prevalent, is carbon.) In a similar manner, Berthollet, in 1787, described this acid in the terms of the phlogistic theory, as consisting of carbon, nitrogen, and hydrogen.—Proust and Ittner discovered many of its compounds. The latter, in 1809, first obtained anhydrous prussic acid from cyanide of mercury and hydrochloric acid, but he regarded its vapour as a permanent gas. Gay-Lussac, in 1811, first obtained this anhydrous acid in the liquid form, and in 1815, determined its quantitative constitution, discovered and examined cyanogen, and thereby gave the principal stimulus to the discovery of many allied compounds.

Cyanogen does not exhibit the characters of a nucleus. It has a peculiar tendency, like chlorine and other inorganic salt-radicals, to unite with 1 At. hydrogen or metal, which is very rarely the case with nuclei. A nucleus, to be converted into an acid, requires the addition of 2, 4, or more atoms of oxygen; for the formation of cyanic acid, on the contrary, 1 At. hydrogen is required in addition to 2 At. oxygen.

The following assumption may, perhaps, serve to reconcile the constitution of cyanogen with the nucleus-theory:—Cyanogen belongs to the series of methylene, C^2H^2. One of the secondary nuclei derived therefrom is prussic acid, C^2NH; and if from this the H be abstracted, there remains cyanogen C^2N. Cyanogen is then an imperfect nucleus of the methylene series, and forms an exception to Laurent's law (p. 19), that if from any nucleus, hydrogen be abstracted without substitution, the remaining compound must belong to the series of another nucleus. In accordance with this assumption, hydrocyanic acid, C^2NH, the metallic cyanides (such as C^2NK), chloride of cyanogen, C^2NCl, &c., must be regarded as secondary nuclei of the methylene-series, and cyanic acid, C^2NH,O^2, as the acid aldide of the nucleus, hydrocyanic acid. Considering the great difference of character between hydrocyanic acid and other organic acids, it will not appear surprising that the former should, according to this view, be regarded as a nucleus, whereas the latter are compounds of nuclei with oxygen. The similarity of hydrocyanic acid to the inorganic hydrogen-acids induces the supposition that the latter, as well as the compounds of 1 At. of a simple salt-radical with 1 At. of a metal, may also be regarded as inorganic nuclei, around which oxygen and other elements group themselves to form oxygen-salts, &c.

Cyanogen is therefore analogous to formyl, C^2H, acetyl, C^4H^3, and other hypothetical radicals of the binary theory; which, according to the nucleus-theory, would be regarded as nuclei from which 1 At. H has been withdrawn.

According to the suggestions on page 37, respecting the arrangement of the atoms in methylene, we must suppose that the four elementary atoms which constitute hydrocyanic acid, the metallic cyanides, chloride of cyanogen, &c., form square tables, two of the diagonally opposite angles consisting of 2 C. When 1 At. hydrogen, metal, chlorine, &c., is withdrawn from these compounds, the N-atom in the residual cyanogen changes its position, placing itself in the middle between the two carbon atoms. It is, perhaps, in consequence of this altered arrangement of the atoms that cyanogen does not easily resume the abstracted atom of hydrogen, metal, chlorine, &c., the restoration being for the most part effected only by substitution.

Cyanogen. C^2N.

Cyan, Blaustoff, Cyanogène; in the gaseous form: *Cyanogen gas.*—Discovered by Gay-Lussac in 1814.—Occurs in the form of hydrocyanic or hydrosulphocyanic acid in a few organic bodies.

Formation. 1. Nitrogen gas passed over charcoal and potash at a strong red heat yields cyanide of potassium.—When nitrogen is passed over a mixture of equal parts of carbonate of potash and pure sugar-charcoal, (which is free from nitrogen,) contained in a porcelain tube kept at a strong red heat—whereupon carbonic oxide passes off at first, but afterwards pure nitrogen—a quantity of cyanide of potassium is found in the carbonaceous residue, such that of 100 pts. of potash used, 12 pts. are converted into cyanide of potassium. The quantity of cyanide of sodium similarly formed from carbonate of soda is much smaller. (Fownes, *J. pr. Chem.* 26, 412.)—Erdmann & Marchand (*J. pr. Chem.* 26, 413) repeated Fownes's experiment with sugar-charcoal and carbonate of

potash. At a moderate red heat, no cyanide of potassium was formed; at a temperature at which potassium-vapour was carried over with the carbonic oxide gas, they obtained only a doubtful trace; but on using carbonate of potash which contained sulphate, the formation of sulphocyanide of potassium was evident.—¶ According to recent communications by Wöhler, (*Jahresber.* 1850, 350, note,) the formation of cyanogen from sugar-charcoal and the nitrogen of the air is established beyond doubt; the essential conditions are, that the temperature be high enough to reduce potassium, and that the nitrogen gas be red-hot.—According to Rieken, (*Ann. Pharm.* 79, 77; *Pharm. Centr.* 1851, 750; *J. pr. Chem.* 54, 133; *Instit.* 1851, 382; *Jahresber.* 1851, 377,) carbonate of potash intimately mixed with charcoal obtained from the purest white sugar, and heated in a current of nitrogen-gas, at a temperature high enough to reduce potassium, is completely converted into cyanide of potassium. In one experiment the conversion was so complete, that the concentrated solution of the cyanide of potassium did not exhibit the least effervescence with acids. When a mixture of potassium or antimonide of potassium (ignited tartar-emetic) and charcoal is heated to full redness in a current of nitrogen, not a trace of cyanide of potassium is formed,—a proof that this formation of cyanogen requires, not only the presence of free potassium, but at the same time a temperature high enough to separate potassium from potash. The formation of cyanogen by igniting a mixture of sugar-charcoal and carbonate of potash has also been confirmed by Delbrück (*Ann. Pharm.* 64, 296) ¶.—The following experiments and observations are less conclusive, as they were made with charcoal containing nitrogen, and therefore the nitrogen required to form the cyanogen may have been derived merely from the charcoal. Nitrogen gas passed through a red-hot mixture of wood-charcoal and carbonate of potash yields a small quantity of cyanide of potassium; air yields less, but still so much that the cyanide of potassium produced from 20 parts of carbonate of potash will form 1 part of prussian blue. (Desfosses, *J. Pharm.* 14, 280.)—This process is used in a manufactory at Newcastle for the preparation of cyanide of potassium on the large scale (*vid. Cyanide of Potassium.*)—A liquid mixture of about equal parts of cyanide of potassium and carbonate of potash has been observed to exude from the cracks of an iron-smelting furnace. (Th. Clark, *Phil. Mag. J.* 10, 729; also *Pogg.* 40, 315; also *J. pr. Chem.* 11, 121.)—At the end of the working of a blast-furnace fed with wood-charcoal and the hot-blast, there was found at the bottom a quantity of carbonaceous matter containing metallic iron, lead, and a saline mass. On immersing this substance in water and leaving it for a month, it was found to be surrounded with a pasty mass smelling of hydrocyanic acid and mixed with crystals of ferrocyanide of potassium, and likewise containing cyanide of potassium and cyanate, carbonate, silicate and manganate of potash, but no chlorine-compound. The cyanate of potash was perhaps formed from the cyanide of potassium by somewhat free access of air during the fusion; the ferrocyanide was probably produced, after the pouring on of the water, from the cyanide of potassium and the iron which was likewise present. It appears then that the nitrogen required to form the cyanogen was supplied from the air. (Zincen & Bromeis, *J. pr. Chem.* 25, 246; also *Pogg.* 55, 89.) The nitrogen might just as well be derived from the charcoal, which is by no means free from that element, inasmuch as wood contains an albuminous substance. (Gm.)—In the iron furnace of Mariazoll in Stiria, which is constructed with closed breast, and is fed with hot air and charcoal,

cyanide of potassium is produced in such quantity that it is sent into the market to be used in galvanic gilding. It is found partly at the light-hole (an aperture from which the gaseous products issue and are set on fire at night for the purpose of illumination), partly in the pipes through which the gases pass. From the light-hole there flows a white salt, which solidifies in stalactitic masses, and consists of cyanide of potassium, cyanate of potash, carbonate of potash, ferrocyanide of potassium, iron, carbide of iron, and charcoal; the same salt coloured grey by charcoal is also deposited above the light-hole. In the tubes which convey the gases from the mouth of the furnace there is formed (doubtless by condensation of the bluish smoke which rises from the furnace when worked by the hot-blast) a black salt, having the same constitution, excepting that carbon and carbide of iron predominate in it. (Redtenbacher, *Ann. Pharm.* 47, 150.)—When a mixture of 2 pts. coke or coal, 2 pts. carbonate of potash and 1 pt. iron filings is ignited in an open vessel exposed to the air, a larger quantity of metallic cyanide is obtained than when an animal charcoal rich in nitrogen is ignited with iron and carbonate of potash in the same proportion in a covered vessel. In this case, 100 pts. of coke yield 17·5 prussian blue. (Thompson, *Athenæum;* also *J. pr. Chem.* 26, 413.) Berzelius asks with reason, whether the nitrogen may not have proceeded from the coal.—¶ Marchand finds that when finely pulverized cast-iron mixed with potassium is ignited, and the aqueous extract treated with ferroso-ferric sulphate and hydrochloric acid, a very abundant precipitate of prussian blue is formed. This effect is produced in even a higher degree with steel, but not with soft iron, or with a mixture of charcoal and pure iron. If an excess of potassium be used, or if the mixture be ignited in an open vessel, no formation of cyanogen takes place. The finely divided iron remaining after the reaction, yielded more cyanogen when again ignited with potassium; whence Marchand concludes that the source of the nitrogen is not in the iron but in the air; in confirmation of which he finds that no formation of cyanogen takes place when the mixture of iron and potassium is ignited in an atmosphere of hydrogen or carbonic acid, but that when the ignition takes place in an atmosphere of nitrogen. an absorption of that gas is apparent. (Marchand, *J. pr. Chem.* 49, 351; *Ann. Pharm.* 66, 245; *Chem. Gaz.* 1850, 301; *Jahresber.* 1850, 324) ¶.

2. Nitric oxide, nitrous acid, and nitric acid, when they act upon organic compounds, even if the latter are free from nitrogen, frequently produce hydrocyanic acid, or hydrocyanate of ammonia, or cyanide of potassium. When a mixture of 1 pt. nitre and 2 pts. purified tartar is thrown into a red-hot crucible, a large quantity of cyanide of potassium is found to have been produced after the deflagration of the mass. (Guibourt, *J. Pharm.* 5, 58.) Nitre, with excess of tartar or acetate of potash, yields cyanide of potassium. (Schindler, *Repert.* 31, 277.) Olefiant-gas, C^4H^4, mixed with access of nitric oxide, and passed through a tube containing heated spongy platinum, brings that metal to a state of intense ignition, and yields water, hydrocyanate of ammonia, carbonic acid [probably in the form of an ammonia-salt], and nitrogen gas. Spongy platinum, when cold, does not act upon a mixture of nitric oxide with excess of alcohol-vapour; but at a red heat, it converts the mixture, with deposition of charcoal, into water, hydrocyanate of ammonia, and carbonate of ammonia. Vapour of nitrous ether (C^4H^5O,NO^3), in which spongy platinum is heated to 400°, yields nitric oxide gas; but if the metal be heated to redness, the products are water, hydrocyanate of

ammonia, carbonic oxide, marsh-gas, and charcoal. (Kuhlmann, *Ann. Pharm.* 29, 284.) A trace of hydrocyanic acid is likewise produced in the combustion of gun-cotton. (Fordos & Gélis, *Compt. rend.* 23, 382.)

Very many organic compounds, both azotized and non-azotized, yield, when heated with dilute nitric acid, a distillate in which a small quantity of hydrocyanic acid may be detected, the nitrogen required for its formation being supplied by the nitric acid, the carbon and hydrogen by the organic body. In this manner, hydrocyanic acid is formed from the following substances: From serum of blood, in large quantity (Fourcroy, *Syst. des connoiss. chim.* 9, 91); Sugar, gum, or starch, in small quantity (Thénard, *Traité*, tom. 4); Alcohol, in the preparation of fulminating mercury (Gaulthier de Claubry, *J. Pharm.* 25, 764) or of nitrous ether, whether the alcohol be heated with nitric acid (Dalpiaz, *N. J. Pharm.* 5, 299) or vapour of hyponitric acid be passed into it (Sobrero); according to Riegel (*Jahrb. f. Pharm.* 20, 143; *Jahresber.* 1850, 350), the formation of hydrocyanic acid in this process takes place only when the distillation is rapidly conducted.—Fats yield a tolerably large quantity (B. Derosne & Chatin, *N. J. Pharm.* 5, 240; Sobrero).—Volatile oils, as the oils of turpentine, juniper, lemon, orange, lavender, valerian, camomile, and cloves, from 1 to 2 per cent. more in proportion as they harden more quickly; moreover, colophony, pine-resin, mastic, copal, and galbanum. (Sobrero.) Hydrocyanic acid is also formed, together with ammonia, when the following vapours are passed through a red-hot tube: Nitrous ether (Thénard), or ether-vapour mixed with nitric oxide or nitrous oxide gas (which, however, produces a dangerous explosion), or vapour of oil of turpentine mixed with nitric oxide gas. (Sobrero, *N. J. Pharm.* 2, 211; 7, 448; also *J. pr. Chem.* 36, 16.) The solution in nitric acid of several compounds of silver-oxide with organic substances, yields, when boiled, a flocculent precipitate of cyanide of silver, which disappears again on further boiling; the less hyponitric acid is evolved on boiling, the greater is the quantity of cyanide of silver precipitated. (Liebig, *Ann. Pharm.* 5, 285.) ¶ Nitric oxide gas passed over the compound of carbonic oxide and potassium heated to redness, forms cyanide of potassium. (Delbrück, *Ann. Pharm.* 64, 296.) ¶

3. Certain nitrogenized compounds give off hydrocyanic acid when distilled with chromate of potash and dilute sulphuric acid. Such, according to Schlieper (*Ann. Pharm.* 59, 1), is the case with gelatin; also, according to Guckelberger, with albumen, fibrin, and casein (*vid.* p. 127.)

4. Ammonia, in contact with organic substances, charcoal, and even with graphite or carbonic oxide gas at a red heat, yields hydrocyanate of ammonia or cyanide of potassium. When ammoniacal gas is passed over charcoal strongly ignited in a porcelain tube, hydrocyanic acid, or rather hydrocyanate of ammonia, passes over into the cooled receiver. (Clouet, *Ann. Chim.* 11, 30; also *Crell. Ann.* 1796, 1, 45; Bonjour, *J. Polytechn. Cah.* 3, 436; also *Scher. J.* 2, 621; Langlois, *Ann. Chim. Phys.* 76, 111; *N. Ann. Chim. Phys.* 1, 117; also *Ann. Pharm.* 36, 64; also *J. pr. Chem.* 23, 232.) In this case, marsh-gas is formed at the same time:

$$4\,NH^3 + 6C = 2(NH^3,C^2NH) + C^2H^4.$$

(Kuhlmann, *Ann. Pharm.* 38, 62.) Ammoniacal gas likewise yields hydrocyanate of ammonia when passed through a red-hot tube, together with carbonic oxide. (Kuhlmann):

$$2NH^3 + 2CO = NH^3,C^2NH + 2HO.$$

A red-hot mixture of charcoal and potash, over which the vapour of ammonia or carbonate of ammonia is passed, is converted, with the utmost ease, into cyanide of potassium. (Desfosses, *J. Pharm.* 14, 280; Kulhmann.) On introducing into the lower part of a gun-barrel closed at the bottom, 100 pts. of buck-horn, and above that a mixture of 50 pts. carbonate of potash, and 25 pts. charcoal, and heating to redness, first the mixture, and then the buck-horn, the mass, when cooled, will yield, with iron-salts, 10 pts. of prussian blue; if, on the contrary, the 100 pts. of buck-horn be mixed with 50 pts. of carbonate of potash and then ignited, only 5·4 pts. of prussian blue will be obtained. If dried ox-blood be used instead of the buck-horn, the product is 20 pts. of prussian blue by the first process, and 11·7 pts. by the second. (Desfosses.)—If the mixture of charcoal and carbonate of potash likewise contain iron filings, ferrocyanide of potassium is formed on passing ammoniacal gas over it. When the ammoniacal vapours evolved on igniting 1000 pts. of bones in an iron retort, are passed over a mixture of charcoal and iron filings saturated with concentrated potash-ley, and heated to redness, 0·86 pts. of prussian blue may be prepared from the product. (Jacquemyns, *N. Ann. Chim. Phys.* 7, 296; also *Ann. Pharm.* 46, 236; also *J. pr. Chem.* 30, 26.)

When an excess of charcoal is ignited in a retort with sal-ammoniac and with lime, or better with litharge (because the litharge does not drive out the ammonia till the heat rises to redness, and perhaps also the excess of it oxidizes 2H of the NH^3), hydrocyanic acid, or rather hydrocyanate of ammonia, distils over (Vauquelin, *Scher. J.* 2, 626; Bucholz, Schrader, *Scher. J.* 628 and 631; Ittner.) Sal-ammoniac ignited with charcoal or graphite and carbonate of potash, produces cyanide of potassium. (Scheele.) In like manner, a very large quantity of cyanide of potassium is obtained by igniting 1 pt. of sal-ammoniac with 8 pts. of crude tartar [which, however, contains nitrogenous ferment]. (Dive, *J. Pharm.* 7, 487.) ¶ Cyanide of potassium is also formed by passing a mixture of carbonic acid and ammoniacal gases, or one of carbonic acid and nitrogen, over heated potassium; also by fusing potassium with lumps of carbonate of ammonia. (Delbrück.) ¶

Formiate of ammonia is resolved by heat into hydrocyanic acid and water. (Döbereiner, p. 276.)

5. All nitrogenous organic compounds, and likewise the azotized charcoal obtained from them, yield large quantities of metallic cyanide, when ignited with a fixed alkali. In this case, while part of the carbon abstracts oxygen from the alkali, 2C and 1N from the organic substance unite with the metal thus freed of the oxygen.—On this reaction is founded the preparation of cyanogen-compounds on the large scale, as well as the detection of small quantities of nitrogen in organic compounds by igniting them with carbonate of potash or with potassium, (pp. 139 and 147.) In manufactories of ferrocyanide of potassium, it is found that the quantity of cyanide of potassium obtained is the same, whether the entire nitrogenous compound be ignited with carbonate of potash, or only the charcoal obtained by igniting it gently in a close vessel. The contrary result might at first be expected, seeing that a large quantity of ammonia is evolved from the entire compound, and this ammonia, according to (4) (*supra*), is also capable of forming cyanide of potassium; but the ammonia is evolved at a temperature much below that at which it can form cyanide of potassium with charcoal and potash. The proportion of cyanide of sodium obtained by igniting carbonate of soda with nitrogenous matters,

is much less than that of cyanide of potassium obtained with carbonate of potash. (Desfosses, *J. Pharm.* 14, 280.)

Preparation. *a. As Gas.* 1. Cyanide of mercury, previously well dried in the water-bath, is heated to commencing redness in a tube or small retort, and the gas collected over mercury. (Gay-Lassac.)—The mercury volatilizes and condenses in the colder part of the apparatus; a small portion of the cyanogen is converted into *paracyanogen*, and remains in the retort, in the form of a brown, loosely coherent mass.—In presence of moisture, a large portion of the cyanogen is decomposed, with formation of ammonia, carbonic acid, and hydrocyanic acid. H. Davy purifies the gas from admixed hydrocyanic acid vapour by agitating it with red oxide of mercury.

2. The gas may likewise be obtained by heating in a retort an intimate mixture of 2 pts. (1 At.) of perfectly dried ferrocyanide of potassium and 3 pts. (1 At.) of corrosive sublimate:

$$2KCy,FeCy + 2HgCl = 2KCl + FeCy + 2Hg + 2Cy.$$

Cyanogen is then evolved, mixed with vapour of mercury, and there remains a dark-coloured mixture of chloride of potassium and cyanide of iron. (Kemp, *Phil. Mag. J.* 22, 179; also *Ann. Pharm.* 48, 100; also *J. pr. Chem.* 31, 63.)

1 At. sulphate of copper might also be mixed with 1 At. cyanide of potassium, with addition of water, and the mixture heated to the boiling point in a gas-generating apparatus; in this case, half the cyanogen present would be given off. But the gas thus obtained is apt to be contaminated with carbonic acid, proceeding from cyanate or carbonate of potash in the cyanide of potassium.

The mode of obtaining cyanogen recommended by Kolb (*Jahrb. d. pr. Pharm.* 10, 311), from ferrocyanide of potassium, black oxide of manganese, and bisulphate of potash, yields, as shown by Harzen-Müller (*Ann. Pharm.* 58, 102), carbonic oxide, carbonic acid, nitrogen, hydrocyanic acid, &c., but *no cyanogen*, and is here mentioned merely with the view of preventing any one from being misled by it.

b. As Liquid. 1. When cyanide of mercury is heated in the longer arm of a strong tube, bent and sealed (I., 286, 287), the cyanogen condenses in the shorter arm, which should be kept cold. (H. Davy & Faraday, *Phil. Trans.* 1823, 196.)—2. Cyanogen gas passed through a tube cooled to a temperature between −25° and −30°, liquefies under the ordinary pressure of the atmosphere. (Bunsen, *Pogg.* 46, 101.)

Properties. Liquid cyanogen freezes at a few degrees below −20°, forming a radiated, icy mass. (Bunsen.) Frozen cyanogen is transparent, crystalline, apparently of the same density as the liquid, and melts at −34·4°. (Faraday, *N. Bibl. univ.* 59, 162.)

Liquid cyanogen is transparent, colourless, and very mobile. (H. Davy & Faraday.) Sp. gr. at 17·2° = 0·866. (Faraday.) Refracting power = 1·316. (Brewster.) Does not conduct the electricity generated by a battery of 300 pairs. (Kemp.)

Tension of Cyanogen expressed in Atmospheres.

According to Faraday.						According to Bunsen.			
at.	Atm.	at.	Atm.	at.	Atm.	at.	Atm.	at.	Atm.
−12·2°	1·53	+6·9°	3·00	+21·1°	4·50	−20·7°	1·00	0°	2·7
6·7	1·89	8·9	3·17	23·3	4·79	20	1·05	+5	3·2
2·8	2·20	10·0	3·28	34·2	6·50	15	1·45	10	3·8
0	2·37	11·1	3·36	35·0	6·64	10	1·85	15	4·4
+3·6	2·72	17·2	4·00	39·4	7·50	5	2·30	20	5·0

According to Niemann, the tension at 12·5 is equal to 4 atmospheres.

A mixture of equal parts of solid and liquid cyanogen (therefore at −34·4°) does not exert a tension equal to the atmospheric pressure. When cyanogen evaporates into the air, an effect which takes place quietly on opening the containing vessel, the remaining portion does not freeze. (Faraday.)

Cyanogen gas is colourless, sp. gr. = 1·8064 (Gay-Lussac); 1·80395. (Thomson.) Refracting power (*vid.* I. 95.) Its odour is somewhat like that of hydrocyanic acid, but at the same time very pungent; in large quantity it is probably poisonous. Combustible.

	Calculation, according to Gay-Lussac.				Vol.		Density.
2 C	12	....	46·15	Carbon-vapour....	2	....	0·8320
N	14	....	53·85	Nitrogen-gas	1	....	0·9706
C^2N	26	....	100·00	Cyanogen-gas	1	....	1·8026

Decompositions. 1. A succession of electric sparks converts 1 vol. cyanogen gas into 1 vol. nitrogen, with separation of charcoal. (H. Davy.)—Cyanogen gas, mixed with hydrogen, undergoes no alteration by the passage of electric sparks. It may be passed without decomposition, either alone or mixed with hydrogen, through a red-hot porcelain tube either empty or filled with copper, gold, or platinum. (Gay-Lussac.)

2. The gas, when set on fire in the air, burns with a carmine-coloured flame: 1 vol. cyanogen gas, mixed with excess of oxygen, and set on fire by the electric spark, explodes violently, with sufficient force, indeed, to break strong tubes, consuming 2 vol. oxygen, and forming 2 vol. carbonic acid and 1 vol. nitrogen, so that the volume of the gas remains unaltered. (Gay-Lussac.)—Cold spongy platinum exerts no action on a mixture of cyanogen and oxygen; but hot spongy platinum becomes ignited, and forms carbonic acid. (Wöhler.) When cyanogen gas mixing with air flows through a heated platinum spiral (II., 46), yellow nitrous vapours are produced. (H. Davy.)—Spongy platinum heated to 291° in a retort filled with a mixture of cyanogen and oxygen, does not act upon it; the action not beginning, indeed, till the heat becomes strong enough to soften glass. (W. Henry.)—Cold platinum-balls (II., 26) do not act upon a mixture of 1 vol. cyanogen gas and 1 vol. detonating gas contained in a tube over mercury. With 2 vol. detonating gas, a slight condensation is apparent; with a larger quantity, a greater condensation; no carbonic acid is, however, produced, but the tube becomes covered with a brownish substance which has an empyreumatic, animal odour, is soluble in water, and gives off ammonia when treated with potash. (W. Henry.) On the other hand, when detonating gas is added to a mixture of 1 vol. cyanogen and 2 vol. oxygen, so that the quantity of oxygen present is sufficient for complete combustion, the spongy platinum immediately causes condensation, if the hydrogen gas in the mixture amounts to more than the cyanogen, nitrous vapours being formed, and 2 vol. carbonic acid produced from 1 vol. cyanogen. (W. Henry, *Ann. Phil.* 25, 419.)—The so-called oxidized sulphide of platinum (VI., 288) absorbs cyanogen gas, producing great development of heat. (Döbereiner.) Cyanogen gas passed through a red-hot tube filled with oxide of copper, is converted into a mixture of 2 vol. carbonic acid and 1 vol. nitrogen. (Gay-Lussac.)

3. *Chlorine gas* does not act upon cyanogen, even in sunshine, if both gases be perfectly dry; but if the gaseous mixture is moist, there is produced, on exposure to sunshine, a yellow oil, which appears to be a

mixture of chloride of carbon and chloride of nitrogen, and often a tolerably large quantity of a white solid substance, having an aromatic odour, insoluble in water, and very sparingly soluble in alcohol and ether. (Serullas, *Ann. Chim. Phys.* 35, 299.)—4. Hypochlorous acid gas slowly decomposes cyanogen gas, with formation of carbonic acid, chlorine, nitrogen, and gaseous chloride of cyanogen; aqueous hypochlorous acid in contact with cyanogen gas, gives off the four gases with effervescence, the liquid afterwards containing hydrochloric and cyanic acid, and being covered with an oily mixture of chloride of cyanogen and chloride of nitrogen. (Balard.)—5. Cyanogen gas in contact with *manganic sulphate* is resolved into carbonic acid and nitrogen. (Berzelius, *Lehrb.*)

6. The *aqueous* solution of cyanogen, which is colourless at first, becomes yellow in a few days, and then brown; deposits brown flakes of azulmic acid; loses its pungent odour, and acquires that of hydrocyanic acid; ultimately contains in solution carbonic acid, hydrocyanic acid, oxalic acid, ammonia, and urea, instead of cyanogen, and sometimes also deposits peculiar crystals. Vauquelin (*Ann. Chim. Phys.* 9, 113; also *Schw.* 25, 50; *Ann. Chim. Phys.* 22, 132; also *N. Tr.* 9, 1, 124) long ago found carbonate and hydrocyanate of ammonia in the decomposed aqueous solution of cyanogen, and likewise obtained crystals of various kinds, which appear to have been partly a mixture of oxalate of ammonia and urea, and partly a peculiar decomposition-product, requiring further investigation. The latter were orange-yellow, transparent, arborescent, inodorous, and tasteless; when heated they gave off water, hydrocyanic acid, and ammonia, and yielded a white sublimate, which appeared to be the same substance in the anhydrous state; they volatilized on red-hot coals, giving off a white fume and a strong ammoniacal odour, and leaving a very small quantity of charcoal; and were not soluble either in water or in dilute acids or potash-ley. These insoluble crystals were deposited from an aqueous solution of cyanogen, which had been left to itself in the winter for some months.—Wöhler (*Pogg.* 15, 627) first pointed out the presence of urea in decomposed aqueous cyanogen; obtained it in abundance by repeatedly saturating the decomposed liquid with fresh cyanogen; and found associated with it two other crystallizable substances, one of which was an ammoniacal salt [oxalate?].—According to Pelouze & Richardson, (*Ann. Pharm.* 26, 63.) an aqueous solution of cyanogen, left to itself in the light, till the odour of cyanogen is no longer perceptible, yields, after filtration from the brown precipitate of azulmic acid, a yellowish, neutral liquid, which smells strongly of hydrocyanic acid; gives off a large quantity of carbonic acid when boiled; then, on further evaporation, evolves hydrocyanic acid and ammonia, and leaves a dry, pale yellow residue, from which alcohol extracts urea, leaving about an equal quantity of oxalate of ammonia undissolved. (Vauquelin's insoluble crystals were not found.) Since, according to Pelouze & Richardson, azulmic acid$=C^6N^4H^4O^4$, therefore$=4Cy+4Aq.$, it may pass over before the commencement of the decomposition which their equation expresses; in that case the equation is as follows:

$$7C^2N + 14HO = 4CO^2 + \underbrace{3C^2NH}_{\text{hydrocyanic acid.}} + NH^3 + \underbrace{NH^4O,C^2O^3}_{\text{oxalate of ammonia.}} + \underbrace{C^2N^2H^4O^2}_{\text{urea.}}.$$

[More simple relations are given by the following equation:

$$10C^2N + 20HO = 4CO^2 + 4C^2NH + \underbrace{C^4H^2O^8}_{\text{oxalic acid.}} + 2NH^3 + \underbrace{2C^2N^2H^4O^2}_{\text{urea.}}.$$

In the action of aqueous ammonia upon cyanogen (p. 388), the decomposition which takes place is,

$$6C^2N + 12HO = 2C^2NH + \underbrace{C^4H^2O^8}_{\text{oxalic acid.}} + \underbrace{2C^2N^2H^4O^2}_{\text{urea.}}.$$

But since, in the decomposition of cyanogen by pure water, 2 At. ammonia must be produced to saturate 1 At. of the bibasic oxalic acid, 4 more atoms of C^2N, together with 8 more At. HO, are resolved into $2NH^3 + 4CO^2 + 2C^2NH$; and these two equations of $6C^2N + 12HO$ and $4C^2N + 8HO$ together make up the above equation of $10C^2N + 20HO$. (Gm.)]—At all events, it must be admitted, that in this reaction two different transformations of cyanogen go on together, the one consisting in the conversion of part of the cyanogen into azulmic acid by assumption of water, the other in the decomposition of the rest of the cyanogen, together with water, into the above-mentioned products.

Cyanogen absorbed by *alcohol* is decomposed in the same manner as that which is absorbed by water, more slowly, however, in proportion as the alcohol contains less water, inasmuch as the water contributes to the decomposition.—*Ether*, saturated with cyanogen, remains unaltered. (Vauquelin.)—Even perfectly anhydrous alcohol, or ether, saturated with perfectly dry cyanogen gas, exhibits the same decomposition as the aqueous solution of cyanogen; after the lapse of 8 months, a brown-black substance is found to be deposited; the cyanogen-odour of the liquid is exchanged for that of hydrocyanic acid; and the solution contains a large quantity of urea, together with the other products mentioned by Pelouze & Richardson. The decomposition goes on more slowly in well-stopped bottles than in vessels which are frequently opened, whence it would appear that the action is accelerated by the oxygen of the air. If the liquid be continually saturated with fresh cyanogen as fast as it is decomposed, a large quantity of urea is obtained, and a considerable amount of cyanogen is required to decompose a small quantity of ether. (Marchand, *J. pr. Chem.* 18, 104.)

7. Cyanogen gas passed over red-hot *carbonate of potash* forms with it a fused mixture of cyanide of potassium and cyanate of potash, the action being attended with evolution of carbonic acid. (Wöhler.)

Aqueous solutions of the fixed alkalis absorb cyanogen gas abundantly, and form first a yellow, then a dark-brown liquid, containing a metallic cyanide, an alkaline cyanate, and an alkaline azulmate. Part of the cyanogen takes up the elements of water, and is converted into azulmic acid, while the remainder produces the two potassium-compounds:

$$2C^2N + 2KO = C^2NK + C^2NK,O^2.$$

The liquid treated with baryta-water neither forms a precipitate which would indicate carbonic acid, nor gives off ammonia; but when the solution is supersaturated with an acid, these two substances make their appearance (Gay-Lussac); for, on the addition of an acid, they are immediately formed from the cyanic acid which is set free. (Wöhler.) Vauquelin found indeed that potash, saturated with cyanogen, evolved ammonia *per se*, the ammonia being perceptible by its odour and its effect on reddened litmus-paper; but, even in this case, it may be regarded as a product of the decomposition of cyanate of potash.

Mercuric oxide acts like the alkalis on aqueous cyanogen. The solution loses its odour, browns the undissolved mercuric oxide by deposition of azulmic acid, and forms a liquid which gives off carbonate of

ammonia when heated, and on evaporation yields crystals of cyanide of mercury, and of another compound, which is perhaps mercuric cyanate. The last-mentioned crystals are transparent four-sided tables, often with truncated edges; they fuse and volatilize on red-hot coals, without decrepitation; give off hydrocyanic acid [proceeding from admixed cyanide of mercury?] when treated with hydrochloric acid; and dissolve in water more readily than cyanide of mercury, forming a solution which does not give any precipitate with potash. (Vauquelin.) Hydrated ferrous oxide also destroys the odour of aqueous cyanogen, assuming a brown, and afterwards a dark-green colour; and, after being separated from the liquid by filtration, dissolves in sulphuric acid, leaving only a small portion of prussian blue; the filtrate, when distilled, gives off hydrocyanate of ammonia, together with a small quantity of carbonate. (Vauquelin.)

8. *Aqueous ammonia* absorbs cyanogen very abundantly, and is decomposed together with it, yielding a brown liquid, which, besides ammonia, contains azulmic, hydrocyanic and oxalic acid, and urea. (Wöhler, *Pogg.* 3, 177; 12; 253.)—Part of the azulmic acid is deposited from the liquid spontaneously, the rest on evaporation. The oxalic acid may be precipitated by lime-water; and the liquid filtered from the lime-precipitate, yields crystals of urea, requiring purification. (Wöhler.) Neglecting the azulmic acid, which is $x(Cy + HO)$, the reaction may be thus expressed:

$$6C^2N + 12HO = \underbrace{2C^2N^2H^4O^2}_{\text{urea.}} + \underbrace{C^4H^2O^8}_{\substack{\text{oxalic}\\\text{acid.}}} + \underbrace{2C^2NH.}_{\substack{\text{hydrocyanic}\\\text{acid.}}}$$

9. Cyanogen gas passed over red-hot *iron* is converted into nitrogen gas, the iron becoming brittle and acquiring a coating of charcoal. (Gay-Lussac.) The solution in acids of the iron thus altered appears to contain ammonia; the carbonaceous mass which remains undissolved, is partially soluble in water, and when ignited with potash yields cyanide of potassium. (Duflos, *Br. Arch.* 22, 282.)

Aqueous cyanogen agitated with iron filings and then set aside, completely loses its odour in 24 hours, then becomes yellowish green, afterwards dark brown, and acquires a pungent, slightly inky taste. If the liquid be filtered after it has lost the greater part of its odour, but before it has acquired any colour, it is found to be rich in iron, and is coloured violet by tincture of galls; on being mixed first with potash and then with an acid, it yields prussian blue; when left to itself, it deposits all the iron in the form of a yellow salt (which is turned blue by sulphuric acid), whilst hydrocyanate of ammonia is the principal substance that remains dissolved in the liquid. If the liquid be not filtered from the iron-filings till the decomposition is complete, the filtrate, when mixed with hydrocyanic acid, becomes first carmine-coloured and then purple; on exposure to the air, it deposits delicate needles, having a pungent taste [urea?]; and, on ignition, leaves a small quantity of ferric oxide, which could not be detected in the filtrate by reagents. The iron-filings on the filter are brown, and when dissolved in sulphuric acid, leave a residue of prussian blue. (Vauquelin.)

Combinations. *a.* With *Water.* Liquid cyanogen does not mix perceptibly with water, but the water turns brown in a few days from decomposition of the cyanogen. (H. Davy & Faraday.)—1 vol. water at 20° gradually absorbs 4·5 vol. cyanogen gas, thereby acquiring a very

pungent taste and odour. (Gay-Lussac.)—The redness, disappearing on the application of heat, which it imparts to litmus paper, Gay-Lussac is inclined to attribute to carbonic acid mixed in small quantity with the cyanogen. For the spontaneous decomposition of aqueous cyanogen, *vid.* pp. 387, 388.

b. With *Hydrogen*, forming hydrocyanic acid.—*c.* With *Hydrogen* and *Oxygen* forming cyanic acid.—*d.* With *Phosphorus ?*—*e.* With *Sulphur* and *Hydrogen*, in various proportions, forming hydrosulphocyanic acid, hydropersulphocyanic acid, hydrosulphocyanogen, &c.—*f.* With *Iodine*, *Bromine*, and *Chlorine*, forming iodide, bromide, and chloride of cyanogen. —*g.* With *Nitrogen?*—*h.* With *Metals*, forming cyanides, which in presence of water may be regarded as hydrocyanates.

i. Cyanogen gas is absorbed to a certain extent by ether, alcohol, volatile oils, and a few other organic liquids.

Hydrocyanic Acid. C^2NH=HCy.

For Literature and History, *vid.* pp. 377, 378.

Prussic Acid, Blausäure, Berlinerblausäure, zootische Säure, Hydrocyan, Hydrocyansäure, Acide prussique, Acide hycrocyanique, Acide cyanhydrique, Acidum borussicum.

The kernels of bitter almonds, peaches, apricots, plums, cherries, and quinces,—the blossoms of the peach, sloe, and mountain-ash,—the leaves of the peach, cherry-laurel, and Portugal laurel,—the young branches of the peach,—the stem-bark of the Portugal laurel and mountain-ash, and the roots of the last-named tree,—when soaked in water and distilled after a while, yield hydrocyanic acid, together with a volatile oil (bitter almond oil). (Bohm, *Schw. J.* 10, 126; Schrader, *A. Gehl.* 1, 392; also *Gilb.* 13, 503; Bucholz, *A. Gehl.* 1, 83; Vauquelin, *Ann. Chim.* 45, 206; also *A. Gehl.* 1, 78; also *Crell. Ann.* 1803, 59; Bergemann, *Schw.* 4, 346; Stöckmann, *N. Tr.* 14, 1, 240, quince kernels; Grassmann, *Repert.* 27, 238; mountain-ash.)—The juice of the root of *Jatropha Manihot* also yields hydrocyanic acid when distilled. (O. Henry and Boutron-Charlard.—But it is only in the moister of these vegetable substances that the acid or any portion of it exists ready formed; the greater quantity is produced during the immersion in cold water, the amygdalin contained in the plants being then resolved, by the action of the emulsin which is also contained in them and acts as a ferment, into grape-sugar, bitter almond oil, and hydrocyanic acid, the last two substances passing over in the distillation. (Robiquet, Liebig, Wöhler.)

¶ The same opinion is maintained by Guibourt, (*N. J. Pharm.* 15, 276,) with regard to the leaves of the cherry-laurel, and now also by Lepage, (*N. J. Pharm.* 15, 274,) although from earlier experiments (*J. Chim. méd.* [3] 4, 365) he was led to the contrary conclusion. Winckler (*Jahrb. pr. Pharm.* 22, 89) maintains that bitter-almond oil containing hydrocyanic acid does really exist in the fresh leaves of the cherry-laurel, small indeed in quantity, and varying with the quantity of water which they contain; but it disappears completely when the leaves are dried. Similarly with the leaves of *Prunus Padus* and *Amygdalus Persica.* ¶

Formation. Several modes of formation have already been given in speaking of cyanogen.—2. In various decompositions of cyanogen and

its other compounds.—3. In the decomposition of fulminates.—4. In the decomposition of formiate of ammonia (p. 276).—5. In the decomposition of amygdalin.

Preparation. A. *In the aqueous state.*—a. *From hydrated ferrocyanide of Potassium.* This salt, which may be regarded as 2KCy,FeCy, 3HO, is decomposed when heated above 100° with sulphuric acid and water, in such a manner that half the cyanogen passes over in the form of hydrocyanic acid, whilst a yellowish white powder, KCy, 2FeCy, is precipitated, and the residual liquid contains sulphate of potash. The best proportion is 2 At. ferrocyanide of potassium to 6 At. sulphuric acid, therefore 2 . 211·4 pts. (=422·8 pts.) ferrocyanide of potassium to 6 . 49 (=294 pts.) oil of vitriol (diluted with any convenient quantity of water),—therefore nearly 10 pts. of the ferrocyanide to 7 pts. oil of vitriol. (Everitt, *Phil. Mag. J.* 6, 97):

$$2(2KCy,FeCy,3HO) + 6SO^3 = 3HCy + KCy,2FeCy + 3(KO,2SO^3) + 3HO.$$

According to this calculation, 422·4 pts. ferrocyanide of potassium yield 3 · 27 (=81) pts. hydrocyanic acid (in the anhydrous state); or 100 pts. ferrocyanide yield 19·16 pts. hydrocyanic acid. Geiger obtained by experiment 17·07, and Wackenroder 17·26.—A larger quantity of sulphuric acid does not act further on the precipitated KCy,2FeCy, and cannot therefore lead to a more abundant evolution of hydrocyanic acid; on the contrary, as it can no longer be taken up by the potash, it decomposes part of the liberated hydrocyanic acid into ammonia and formic acid, and consequently the hydrocyanic acid which distils over is smaller in quantity and contaminated with formic acid. It is better indeed to reduce the quantity of sulphuric acid to one-half (3·5 pts. oil of vitriol to 10 pts. ferrocyanide of potassium), so that monosulphate of potash may be formed instead of bisulphate; as, however, the monosulphate is but sparingly soluble, and is therefore deposited in the cyystalline form during the distillation, it increases the percussive ebullition caused by the white crystalline powder, so that drops of the mixture are often thrown up, and mix with the distillate. Hence it is good to throw a few clippings of platinum-foil into the mixture. (I. 276.)

The greater part of the hydrocyanic acid goes over in the beginning of the distillation at a temperature somewhat above 100°; and when the residual liquid attains a higher temperature, the water follows, containing but little hydrocyanic acid. A good condensing apparatus is therefore necessary; otherwise the hydrocyanic acid which passes over at first—since its boiling point is not above 27°, will for the most part escape in vapour together with the air of the apparatus. Water in the receiver likewise tends to prevent this loss.—It is not necessary to boil the residue down to dryness; it is sufficient indeed to distil off from $\frac{2}{3}$ to $\frac{3}{4}$ of the liquid, according to the quantity of water present.

The sulphuric acid used is common English oil of vitriol, free from nitric acid. There is no advantage in distilling the ferrocyanide of potassium with phosphoric instead of sulphuric acid; on the contrary, as the strength of a solution of phosphoric acid is very variable, it is less easy to determine the exact quantity required than with oil of vitriol.

It is unnecessary to dissolve the ferrocyanide in water before adding the sulphuric acid, as it readily dissolves in the water as the distillation goes on.

The distillatory apparatus must be so arranged as to prevent any portion of the mixture from spirting over—to contain but little air, inas-

much as the air in escaping always carries hydrocyanic acid vapour with it—and to present the greatest possible amount of cooling surface.

If the distillate should become contaminated with sulphate of potash and prussian blue by spirting, it must be carefully rectified over a small quantity of magnesia, carbonate of lime, or carbonate of baryta, in an apparatus affording ready means of condensation. This however occasions loss of hydrocyanic acid, and the rectified acid is much more liable to spontaneous decomposition. (Kemmerich, *Br. Arch.* 12, 92 ; Duflos, *Kastn. Arch.* 14, 114.)

The following mode of conducting the process may be depended upon for giving satisfactory results: 10 parts of coarsely pounded ferrocyanide of potassium are introduced into a flask, together with a cooled mixture of 6 pts. oil of vitriol and between 30 and 40 of water, and a few clippings of platinum; and the bent tube *b* (*App.* 51) is fitted into the flask, its shorter arm, which is not quite upright, being blown out to a bulb in the middle, so as to prevent any contamination of the distillate by matter spirting up from the flask, and its longer arm, which is 3 feet long and descends gradually, being covered with a long narrow strip of paper, kept constantly wet by means of the dropping bottle. (*App.* 36.) The end of this long arm is fitted by means of a cork into the neck of a tubulated receiver *c*, (*App.* 51,) which, if very strong hydrocyanic acid is to be obtained, must be empty and surrounded with ice, but in the contrary case must contain water and be surrounded with ice or with cold water. In either case, a Welter's safety-tube is fitted into the tubulus of the receiver to convey the escaping air into a long-necked flask containing water, which retains the rest of the hydrocyanic acid. The distillation is continued till the residue is reduced to one-fourth of the original quantity, and in this manner, the acid is obtained with scarcely any loss, even in summer. (Gm.)

The following are other modifications of the process:

10 pts. ferrocyanide of potassium, 3·75 oil of vitriol and 40 water, distilled till 10 pts. of distillate are obtained. (Scheele.) If no hydrocyanic acid were lost, the distillate should by calculation contain 19·16 per cent. of anhydrous acid.

10 pts. ferrocyanide of potassium, 5 oil of vitriol, and 10 water. (Ittner.) The same strength, provided the distillation be carried nearly to dryness.

10 pts. ferrocyanide of potassium dissolved in 40 pts. of warm water; 8·9 oil of vitriol [too much] mixed with 19 water; in the receiver, 20 parts of water, distilled till the liquid in the receiver amounts to 60 pts. (Giese, *Scher. Ann.* 2, 337.) Should contain 3·27 per cent. of hydrocyanic acid.

10 pts. ferrocyanide of potassium dissolved in 40 pts. of hot water; mixed with 6 pts. oil of vitriol and 6 water, and distilled in the chloride of calcium bath from a retort having its neck slightly inclined upwards, and connected with a Liebig's condensing tube, (I. 288,) which reaches to the bottom of a tall, narrow-necked cylinder, containing 50 pts. of cold water. The mixture is distilled till the 50 pts. water are increased to 95 (Geiger & Hess, *Ann. Pharm.* 3,318.) [According to calculation, this acid should contain 2·06 per cent. of anhydrous prussic acid.]

10 pts. pulverized ferrocyanide of potassium, 12 oil of vitriol [too much] mixed with 20 water; 72 water in the receiver; 16 pts. distilled over, so that the whole amounts to 88; neck of retort slanting upwards and connected with a long tube, which is bent downwards at a short

distance from the retort, and kept cool, &c. The distillate contains traces of formic and sulphuric acid. (Wackenroder, *N. Br. Arch.* 29, 35. —According to calculation, this distillate should contain 2·17 per cent. of anhydrous prussic acid.

10 pts. ferrocyanide of potassium, 5 oil of vitriol and 125 water; 31 water in the receiver; apparatus like Wackenroder's; retort heated in the chloride of calcium bath to 125°; the distillate mixed with a quantity of water sufficient to make it up to 114 pts.; lastly, 3 drops of oil of vitriol added to render the hydrocyanic acid more permanent. (Thaulow, *J. pr. Chem.* 31, 252.)—The addition of oil of vitriol interferes with the use of the acid in many cases. According to Thaulow, the acid thus prepared contains 1·5, by calculation 1·68 per cent. of anhydrous prussic acid.

¶ 10 pts. ferrocyanide of potassium, 5 oil of vitriol, and an adequate quantity of water, yield, when distilled to dryness, from 57 to 59 per cent. of the quantity of hydrocyanic acid corresponding to the cyanogen in the cyanide of potassium; if the distillation be performed in a current of aqueous vapour, 86·49 p. c. pass over. 3 pts. ferrocyanide and 2 oil of vitriol twice distilled with a proper quantity of water, yield 85·6 per cent. of the acid corresponding to the cyanogen in the cyanide of potassium; on repeating the distillation four times, the quantity of hydrocyanic acid obtained rather exceeded that which corresponded to the cyanide of potassium; the residual sediment amounted to 21·16 p. c. of the salt; and the filtrate contained a ferric salt. We cannot therefore exactly determine how much of the cyanogen in the ferrocyanide is converted into hydrocyanic acid, inasmuch as this quantity is effected by the mode of distillation. In preparing the medicinal acid, the strength must be determined by analysis. (Mohr. *Arch. Pharm.* [2], 55, 11; *Jahresber.* 1847–8, 474.) ¶

Comp. Göbel (*N. Tr.* 5, 2, 22).—Schroder (*Berl. Jahrb.* 22, 83; 27, 2, 73; *Br. Arch.* 2, 59).—Trommsdorff (*Taschenb.* 1822, 209).—Grischow (*Schw.* 33, 325).—Strathing (*Repert.* 25, 159).—Neuhaus (*Br. Arch.* 7, 71).—Duflos (*Kastn. Arch.* 14, 11; *Br. Arch.* 29, 65).—Brandes, *Br. Arch.* 2, 74, and 261).—Trommsdorff, Jun. (*N. Br. Arch.* 11, 216).

b. From Cyanide of Potassium.—This compound is so far better adapted for the preparation of hydrocyanic acid, that it is decomposed by acids at medium temperatures, into a potash-salt and hydrocyanic acid; but there is greater difficulty in obtaining it in a uniformly pure state, and consequently in determining with accuracy the quantity of hydrocyanic that it will yield,—a point of essential importance in the preparation of the medicinal acid.

1. Ferrocyanide of potassium perfectly dehydrated and then heated to redness in a well-closed iron or earthen crucible, yields a mixture of cyanide of potassium and carbide of iron. Robiquet (*J. Pharm.* 17, 653) distils the filtered aqueous solution of this mass with sulphuric acid. Gautier (*J. Pharm.* 13, 17) introduces the perfectly black mixture, coarsely pounded, into a retort, through the tubulus of which water and hydrochloric acid [or better, dilute sulphuric acid] are poured in by means of an S-tube. As the hydrocyanic acid is given off abundantly, even at a very gentle heat, the heat must be very cautiously applied, and good means of condensation provided. (*Comp.* Boudet, *J. Pharm.* 20, 531.)

2. A solution of 1 pt. of cyanide of potassium prepared by fusing the ferrocyanide with carbonate of potash, in 2 pts. water, is put into a distillatory apparatus, a cooled mixture of 1 pt. oil of vitriol and 3 water added by small portions, waiting before each addition till the efferves-

cence caused by the last has subsided; and the mixture distilled at a gentle heat. (Liebig.) Since cyanide of potassium, prepared in the manner just mentioned, contains 1 At. cyanate of potash for every 5 At. of the cyanide, and the cyanic acid liberated therefrom is quickly resolved into carbonic acid and ammonia, the addition of sulphuric acid produces evolution of carbonic acid, and the residue of the distillation consists of sulphate of potash and sulphate of ammonia. 2 At. ferrocyanide of potassium directly distilled with sulphuric acid, yield only 3 At. hydrocyanic acid; but when previously converted into cyanide, they yield 5 At. of the acid. (Liebig, *Ann. Pharm.* 41, 288.) Part of the hydrocyanic acid is lost by being carried away with the carbonic acid. It is also doubtful whether the acid thus prepared will keep, since carbonate of ammonia may be formed in it from the small quantity of cyanic acid which passes over in the distillation.

3. To a solution of 9 pts. tartaric acid in 60 pts. water, contained in a well-stoppered bottle nearly filled with it, 4 parts of pure cyanide of potassium are added; the vessel shaken, frequently dipped into cold water, and then left in the cold for 12 hours; and the aqueous hydrocyanic acid, which contains but a very small quantity of tartrate of potash, poured off from the crystallized tartrate. (Th. Clarke, *Lond. med. surg. J.* 6, 524; also *J. chim. méd.* 7, 544.)—According to calculation, this acid contains 3·6 per cent. of anhydrous prussic acid.

c. From Cyanide of Mercury.—1. Cyanide of mercury is agitated with iron filings, sulphuric acid, and water, in a well-stoppered bottle. till the liquid no longer tastes of mercury [or better, till a portion of it taken out is no longer blackened by sulphuretted hydrogen], the solution then decanted from the iron and mercury into a retort, and distilled. (Scheele.)—In this process, the oxygen of the water unites with the iron, for the formation of ferrous sulphate, the hydrogen with the cyanogen, forming hydrocyanic acid, and the mercury is separated in the metallic state:

$$HgCy + Fe + HO + SO^3 = FeO,SO^3 + HCy + Hg.$$

According to this equation, 126 pts. cyanide of mercury require 49 pts., or rather more, of oil of vitriol, together with a considerable quantity of water, and at least 28 pts. of iron filings; an excess of iron, however, accelerates the decomposition. If the cyanide of mercury be carefully weighed, this method is very well adapted to produce an acid of definite strength. The acid distils over at a gentle heat. (Gm.; *comp.* Duflos, *Kastn. Arch.* 14, 113.)

3. Sulphuretted hydrogen is passed through an aqueous solution of cyanide of mercury as long as it is absorbed, and the solution separated by filtration from the sulphide of mercury. (Proust, Vauquelin.)

$$HgCy + HS = HgS + HCy.$$

Vauquelin, who employs a solution of 1 pt. cyanide of mercury in 8 pts. water, frees the solution from excess of sulphuretted hydrogen by agitation with carbonate of lead, till fresh portions of that salt are no longer browned by it, and filters the liquid again. But even if these filtrations be performed in a well-covered filter, a considerable quantity of prussic acid is lost by evaporation, so that this process never yields an acid of definite strength; mereover, the acid thus prepared is apt to be somewhat contaminated with hydrosulphocyanic acid and oxide of lead.—*Comp.* Schröder. (*Berl. Jahrb.* 22, 97; *Br. Arch.* 2, 59.)

d. From Cyanide of Silver.—Cyanide of silver precipitated from the nitrate by hydrocyanic acid is washed and dried; 200 pts. of it shaken up with 240 pts. hydrochloric acid of sp. gr. 1·129, and when the decomposition is complete, the hydrocyanic acid is separated from the chloride of silver by decantation. (Everitt, *Phil. Mag. J.* 6, 100.)—This hydrocyanic acid may contain a small quantity of hydrochloric acid, but has the advantage of definite strength.

e. From Cyanide of Lead.—The cyanide precipitated from sugar of lead by prussic acid is decomposed by an equivalent quantity of dilute sulphuric acid. (Thomson.) As, however, the cyanide of lead is difficult to dry, the quantity of sulphuric acid required cannot be exactly determined; if too little be used, lead remains in solution. (Soubeiran, *N. J. Pharm.* 1, 121.)

f. Hydrocyanic acid of perfectly definite strength can only be obtained by mixing weighed quantities of the anhydrous acid and water.

B. *Preparation of Anhydrous Hydrocyanic Acid.*—The great volatility and highly poisonous character of hydrocyanic acid render this process very dangerous; it should, therefore, only be performed in winter, and with the aid of freezing mixture.

a. A strong aqueous solution of prussic acid is prepared by one of the preceding processes, and the water removed from it by chloride of calcium. Trautwein (*Repert.* 11, 13) distils 15 pts. of ferrocyanide of potassium with 9 pts. oil of vitriol and 9 pts. water, till 4 or 5 pts. of strong acid have passed over into the receiver, which must be surrounded with ice or with a mixture of ice and salt; pours the acid into a strong bottle provided with a good stopper and kept cold by a freezing mixture; and adds pulverized chloride of calcium in small successive portions, and with frequent agitation, so that no great development of heat may take place. The mixture, after being left at rest for a while, separates into two layers, the lower one consisting of aqueous chloride of calcium, and the upper of hydrocyanic acid freed from part of the water. The acid is then poured into another bottle, and again treated with chloride of calcium; and this treatment continued till fresh quantities of chloride of calcium added to the acid no longer become pasty and cake together, but remain pulverulent. By this treatment, Trautwein obtains from 2 to 2¼ pts. of anhydrous acid.—[Since a considerable quantity of acid is lost at each decantation, and moreover the vapour which escapes may exert a poisonous action, it is better to leave the acid in the first bottle and draw off the solution of chloride of calcium by a syphon. This syphon is filled with a saturated solution of chloride of calcium, closed with the finger at the end of the longer arm, and not opened till the shorter arm is depressed to the lowest part of the bottle held in a somewhat inclined position. As soon as the chloride of calcium solution has completely run out, the syphon is again closed with the finger and taken out. More chloride of calcium is then introduced, &c., &c. As soon as a fresh portion of that substance no longer becomes pasty, the acid may be decanted into a well-cooled bottle containing pulverized chloride of calcium, and finally into a clean bottle. (Gm.)]

b. Vapour of strong prussic acid evolved from a mixture, is passed immediately over chloride of calcium, which retains the water.

1. The concentrated and filtered solution of the black mixture of cyanide of potassium and carbide of iron left after ignition of the ferrocyanide (p. 392), is distilled, and the vapour passed through a tube filled

with chloride of calcium into a cooled receiver. (Robiquet, *J. Pharm.* 17, 653.)

2. The black mixture just mentioned is put into a tubulated retort and moistened with water; hydrochloric acid poured in through an S-tube; and the evolved hydrocyanic acid (according to Gay-Lussac's method) passed through a tube, the fore part of which contains pulverized marble (to retain the hydrochloric acid), and the hinder part, chloride of calcium (to retain the water), and thence through a knee-shaped tube into a bottle surrounded with ice. (Gautier, *J. Pharm.* 13, 17.)

3. A mixture of 8 pts. ferrocyanide of potassium, 3 pts. burnt tartar, and 1 pt. charcoal is fused in a covered crucible; the fused mass digested with 6 times its weight of water in a vessel which can be closed; and the clear solution decanted from the sediment of iron and charcoal into a tubulated retort, which is connected with a glass tube horizontal in the nearer part, bent downwards at a certain distance from the retort, and passing into a U-tube. This U-tube is placed within a cylinder containing cold water, and is filled with chloride of calcium, excepting at the end where the vapours enter, and at this end are placed small pieces of the fused mixture above mentioned. The other end of the U-tube is connected by a bent tube with the glass, which serves as a receiver, and is surrounded with ice, or better, with a freezing mixture. A cooled mix- of 1 pt. oil of vitriol (the fused mixture whose solution is contained in the retort being supposed = 2) and 1 pt. water is then poured into the retort by small portions at a time, through a funnel-tube adapted to the tubulus. The mixture starts spontaneously into strong ebullition, so that the sulphuric acid must be added slowly, and the greater part of the hydrocyanic acid distils over without the application of heat. Finally, when all the sulphuric acid has been added, and the boiling has ceased, the retort is heated till the contents begin to boil gently; and the cylinder in which the chloride of calcium tube is immersed, is emptied of cold water and filled with water at 30°—35°, to volatilize the prussic acid there condensed, and cause it to pass over into the receiver. (Wöhler, *Berzelius Lehrb.* 1, 816.)

The mixture of 8 pts. ferrocyanide of potassium, 3 pts. burnt tartar, and 1 pt. charcoal, forms, after ignition, not a fused mass, but a coarse powder. That part of it which is introduced into the nearer end of the U-tube is converted, by the first portions of water that pass over, into a mud which stops up the U-tube, and thereby causes the liquid in the retort to spirt up through the funnel-tube. And even if the U-tube contains nothing but lumps of chloride of calcium, the large quantity of water which passes over quickly liquefies the chloride of calcium, and consequently the process must be interrupted when only a small portion of the acid has passed over. For this reason, it might be advisable to use a smaller quantity of water to dissolve the ignited mass. On the whole, perhaps Trautwein's method of dehydration is the best, although it may perhaps be found preferable, in preparing the hydrated acid, to use Wöhler's mixture instead of the ferrocyanide of potassium. (Gm.) ¶ To obviate these objections, Wöhler now recommends that the neck of the retort be inclined upwards at an angle of about 45°, and an intermediate vessel containing a small quantity of chloride of calcium or cyanide of potassium placed between the retort and the U-tube. The chloride of calcium tube and the intervening vessel are immersed from the beginning of the operation in water at 30°, and the prussic acid vapour is condensed in a tall narrow vessel, surrounded with a mixture of ice and salt; the acid

is then obtained in the crystallized state. The cheapest mode of preparing anhydrous prussic acid is by the direct decomposition of ferrocyanide of potassium, viz., by distilling in the apparatus just described, a mixture of 10 pts. of that salt with 7 pts. oil of vitriol and 14 water; the funnel-tube may then be dispensed with. The mixture boils regularly and without percussion over an open charcoal fire. (*Ann. Pharm.* 73, 218; *Jahresber.* 1850, 350.) ¶

4. Cyanide of mercury is gently heated with aqueous hydrochloric acid in a retort, the neck of which is connected with a tube 0·6 met. long and 0·01 met. wide. In the first third of this tube are placed fragments of marble, and in the other two-thirds small pieces of fused chloride of calcium. The tube passes into a receiver surrounded with ice or with a freezing mixture. The prussic acid which condenses in the marble and the chloride of calcium, is gradually driven into the receiver by gently heating the tube from the end next the retort to the other end. (Gay-Lussac.) Ittner proceeded in the same way, excepting that he received the vapour of the prussic acid over mercury. If the hydrochloric acid is in excess, part of the evolved hydrocyanic acid is converted into ammonia (and formic acid), so that sal-ammoniac is found in the residue, together with the corrosive sublimate. (Vauquelin.) Hence the quantity of hydrochloric acid used must not be greater than that which is absolutely required to effect the decomposition. (Pelouze.)—126 pts. cyanide of mercury require, to decompose them, 179 pts. hydrochloric acid of sp. gr. 1·10, or 126 pts. of sp. gr. 1·16, or 94 pts. of sp. gr. 1·19.)—P. v. Schulz (*Scher. Ann.* 6, 310) condensed the hydrocyanic acid evolved from 6 ounces of cyanide of mercury and 4 ounces of hydrochloric acid in a second tubulated retort, filled with a mixture of chloride of calcium and carbonate of lime, and kept cold,—and then immersed this second retort, after closing the tubulus, in water at 37·5°,—whereupon there passed over at first a drachm of transparent and colourless prussic acid, which did not congeal at −37·5° (Gay-Lussac's acid froze at −15°), remained unaltered for a week at −25°, but at −10° was soon converted, without loss of weight, into a dry, black substance. [Did it contain much ammonia ?]

c. The hydrocyanic acid is evolved directly in the anhydrous state.—Vauquelin passes dry sulphuretted hydrogen gas in a slow current through a tube filled with dry pulverized cyanide of mercury—except at the farther end, where there is placed a small quantity of carbonate of lead—and connected with a receiver surrounded with ice and salt. The process is stopped as soon as the carbonate of lead begins to blacken, indicating that sulphuretted hydrogen is about to pass into the receiver.

Testing of Hydrocyanic Acid, especially of the Hydrated Acid.

The acid should be transparent and colourless; should not redden litmus, or if it does, the reddening ought to be feeble and transient; and should evaporate at 100° without leaving a residue.

Strength.—1. Determining the specific gravity does not afford an exact estimation of the strength. (Ure, *Schw.* 36, 282.)—2. To a weighed quantity of the aqueous acid a weighed quantity of finely powdered red oxide of mercury is added, by small portions and with agitation, till the last portions added remain undissolved, and the odour of hydrocyanic acid is no longer perceptible. The weight of the remaining quantity of

mercuric oxide deducted from the original weight, gives the weight of the quantity dissolved; and since 108 pts. of mercuric oxide require for solution 27 pts. of anhydrous prussic acid, it follows that 4 pts. of mercuric oxide dissolved indicate the presence of 1 pt. of anhydrous acid in the liquid under examination. (Ure, *Quart. J. of Sc.* 13, 321; also *Schw.* 36, 282.) As the cyanide of mercury thus formed is capable of taking up more of the mercuric oxide, even at ordinary temperatures, forming, indeed, the compound HgO,HgCy; this method is apt to give too great an amount of hydrocyanic acid, especially if the liquid be not kept cool, and the addition of mercuric oxide stopped as soon as the odour of hydrocyanic acid has disappeared. Moreover, it must first be ascertained that the prussic acid to be examined is free from hydrochloric acid, which would likewise dissolve mercuric oxide. In this case Geoghegan saturates the hydrochloric acid with carbonate of lime before adding the mercuric oxide.—This method is not applicable to cherry-laurel water, bitter almond water, &c., because these waters contain a vegetable acid, probably benzoic acid, which likewise dissolves mercuric oxide. (Duflos, *Kastn. Arch.* 14, 88.)—3. Nitrate of silver mixed with a small quantity of ammonia, such that the liquid, after precipitation, may be rather acid than alkaline, is dropped into the hydrocyanic acid, as long as any precipitate of cyanide of silver is produced; the precipitate collected on a small filter previously dried at 100° and weighed; and the precipitate and filter washed and dried together at 100° and weighed.—134 pts. of cyanide of silver indicate 27 pts. of anhydrous prussic acid.—The acid may also be precipitated by a mixture of nitrate of silver and ammonia, and nitric acid then cautiously added to the liquid till a slight acid reaction is produced. (Duflos.) This method is the most accurate of all. ¶ 4.—1 At. cyanide of potassium forms, with 1 At. cyanide of silver, a soluble double cyanide which is not decomposed by excess of alkali. If then a liquid containing hydrocyanic acid be mixed with solution of caustic potash till a strong alkaline reaction is produced, and then with a graduated solution of nitrate of silver till the liquid begins to show turbidity, 1 At. of silver used will correspond exactly to 2 At. hydrocyanic present in the liquid. The presence of formic or hydrochloric acid has no influence on the result. This method is quite as accurate as the last, and is applicable to bitter almond water and laurel water, as well as to medicinal prussic acid. Bitter almond water, which is turbid from the presence of oily drops, must first be mixed with three or four times its bulk of water to render it clear; otherwise the limit of the reaction will not be seen. (Liebig, *Ann. Pharm.* 77, 102; *Pharm. Centr.* 1851, 334; *N. J. Pharm.* 19, 297; *Chem. Soc. Qu. J.* 4, 219.) ¶—5. Mercurous nitrate is added to the hydrocyanic acid, and the quantity of metallic mercury thereby precipitated ascertained. As the reaction which here takes place is:

$$HCy + Hg^2O = HgCy + HO + Hg,$$

it follows that 100 pts. (1 At.) mercury indicate the presence of 27 pts. (1 At.) of hydrocyanic acid. According to Jahn, this mode of determination is less exact, and gives too little hydrocyanic acid; because the nitric acid which is set free redissolves a portion of the precipitated mercury [and because the mercury-solution may likewise contain mercuric nitrate].—6. The hydrocyanic acid is mixed, first with potash, then with a ferroso-ferric salt, then with excess of hydrochloric acid, and the weight of the resulting prussian blue determined in the same manner as that of the cyanide of silver in (3), excepting that the filter, and the

precipitate and filter together, must be dried at a temperature not exceeding 30°—40°. In this process, 610 pts. of prussian blue (regarded as $Fe^7Cy^9,20HO$) indicate 243 pts. of hydrocyanic acid = 100 : 40 (according to Ittner, 100 pts. prussian blue correspond to 48 hydrocyanic acid). The determination is, however, uncertain, inasmuch as prussian blue contains variable quantities of water and ferrocyanide of potassium.

Contamination with Sulphuric, Hydrochloric, Nitric, Tartaric, and other of the stronger Acids.—1. Tincture of litmus is strongly reddened by the acid thus contaminated, and retains its red colour after a day's exposure to the air.—2. Hydrocyanic acid contaminated with a stronger acid, throws down red iodide of mercury from the colourless solution of the compound of cyanide of mercury with iodide of potassium. That this test may give correct results, however, the hydrocyanic acid must be free from alcohol, because that liquid would retain the iodide of mercury in solution. (Geoghegan. *Phil. Mag. J.* 7, 400; also *J. pr. Chem.* 7, 99.)

Contamination with Sulphuric Acid.—Turbidity with chloride of barium.

With Hydrochloric Acid.—As the cyanide of silver precipitated by hydrocyanic acid from nitrate of silver is very much like the chloride obtained with hydrochloric acid, the following distinctive tests are required besides those above mentioned.—1. The acid mixed with ammonia and evaporated on the water-bath, leaves a residue of sal-ammoniac, the hydrocyanate of ammonia passing off in vapour.—2. When a small quantity of borax is dissolved in the acid, and the liquid evaporated to perfect dryness; the aqueous solution of the residue gives a precipitate with nitrate of silver, if the acid originally contained hydrochloric acid. (Wackenroder.)—3. The precipitate obtained with excess of nitrate of silver does not dissolve completely in warm concentrated nitric acid, if it contains chloride of silver as well as cyanide. (Liebig, *Ann. Pharm.* 18, 70.)

With Sulphuretted Hydrogen.—Brown precipitate with solution of cyanide of mercury.

With Ammonia.—Prussic acid thus contaminated, soon turns brown; treated with strong potash in the cold, it gives off ammonia, recognizable by the cloud which it forms with hydrochloric acid; evaporated with a small quantity of bisulphate of potash, it leaves a residue containing ammonia.

With Oxide of Lead.—This impurity is found in Vauquelin's prussic acid; it may be recognized by the precipitates which it forms with sulphuretted hydrogen and sulphuric acid.

With Cyanide of Mercury.—This impurity is present in the acid prepared by Vauquelin's method, if the current of sulphuretted hydrogen has not been continued long enough.

With Formic Acid.—May be present when the acid has been prepared by distilling a cyanide with excess of sulphuric or hydrochloric acid. It causes the acid to redden litmus, although no hydrochloric or sulphuric acid is present. On dissolving mercuric oxide in the acid and heating the solution, the mercury is reduced, producing a grey cloud and a precipitate of mercurial globules. (Wackenroder.)—If the greater part of the liquid be evaporated at a gentle heat, the residue reduces mercuric oxide with effervescence. (Geiger.)—200 pts. of mercury thus precipitated indicate the presence of 46 pts. of formic acid.—By digesting the acid

thus contaminated with carbonate of lead, and evaporating the filtrate, needles of formiate of lead are obtained.

With Hydrosulphocyanic Acid.—In Vauquelin's acid, a few drops of a ferric salt produce a deep red colour.

A residue left after evaporation of the acid over the water-bath, may consist of: Phosphoric or sulphuric acid, sulphate of potash, prussian blue, bitartrate of potash, oxide of lead, cyanide of mercury.

Properties of Anhydrous Hydrocyanic Acid.—Transparent, colourless, mobile liquid. Freezes at $-15°$, forming a fibrous crystalline mass. (Gay-Lussac.) Specific gravity of the acid prepared according to B, *b*, 4, p. 395, = 0·70583 at 7° and 0·6969 at 18° (Gay-Lussac); of that obtained by the process B, *a*, p. 394, = 0·705 .... 0·710 at 6° (Trautwein); of the acid obtained from cyanide of mercury by sulphuretted hydrogen (B, *c*, p. 396), 0·706 at 2·8° (Cooper.) Refracting power 1·275. (Cooper, *Phil. Mag. J.* 14, 186.)—Boils at 26·5° (Gay-Lussac), at 27·5....29°. (Trautwein.) Tension at $+ 10° = 0·38$ met. Hydrocyanic acid evaporating in a constant quantity of air at + 20°, increases its volume five times. A drop of the acid evaporating in the air on a glass rod or on paper, produces a degree of cold by which the remaining portion is frozen. Sp. gr. of the vapour = 0·9746. (Gay-Lussac.) Refracting power of the vapour (I., 95). The feeble [tolerably strong] reddening of litmus produced by this acid, disappears as the acid evaporates in the air. (Gay-Lussac.)

Hydrocyanic acid has a very powerful odour resembling that of bitter almonds; its taste is cooling at first, but afterwards bitter and pungent. The vapour when inhaled excites coughing, giddiness, and head-ache. This acid destroys life more quickly than any other narcotic poison, the quantity of the real acid required to produce fatal effects being smaller as the acid is less diluted with water.—Since a trace of hydrocyanic acid prevents the oxidation of sugar (but not that of albumen or fibrin) by iodic acid (p. 126), the poisonous action of the acid may perhaps arise from its interfering with the oxidation, by the respiratory process, of various substances contained in the blood; ferrocyanide of potassium, which does not prevent the oxidizing action of iodic acid, is likewise destitute of poisonous properties. (Millon, *N. Ann. Chim. Phys.* 13, 40.)

Hydrocyanic acid forms a white, curdy precipitate with nitrate of silver; when mixed with potash, then with a ferroso-ferric salt, and then with excess of hydrochloric acid, it yields prussian blue.

¶ Mixed with sulphide of ammonium and gently heated till the mixture becomes colourless, it yields a liquid containing sulphocyanide of ammonium, which gives with ferric salts a very strong blood-red colour, and with cupric salts, in presence of sulphurous acid, a white precipitate of cuprous sulphocyanide. (Liebig, *Ann. Pharm.* 61, 127; *Phil. Mag. J.* 31, 140; *Jahresber.* 1847-8, 987.)—This is an extremely delicate test. According to A. Taylor, (*Ann. Pharm.* 65, 263,) it will show distinctly the presence of $\frac{1}{3050}$ of a grain of anhydrous prussic acid in a very dilute liquid, whereas the prussian blue test is not capable of detecting less than $\frac{1}{750}$ of a grain. The best mode of applying the test, according to Taylor, is to place the liquid containing the hydrocyanic acid in a watch-glass, and cover it with another which is moistened with a drop of sulphide of ammonium. After a few minutes, the upper watch-glass is gently heated till the sulphide of ammonium is dry, and the dried residue is treated with sesquichloride of iron. ¶

	According to Gay-Lussac.		Thomson. *Ann. Chim. Phys.* 8, 434.	Porret. *Schw.* 17, 300.
2 C	12	44·45	42·51	34·8
N	14	51·85	46·37	40·7
H	1	3·70	11·12	24·5
C^2NH	27	100·00	100·00	100·0

	Vol.	Density.		Vol.	Density.
Carbon-vapour	2	0·8320	Cyanogen gas	1	1·8026
Nitrogen gas	1	0·9706			
Hydrogen gas	1	0·0693	Hydrogen gas	1	0·0693
Prussic acid vapour	2	1·8719	Prussic acid vapour	2	1·8719
	1	0·9359		1	0·9359

Decompositions. 1. Vapour of hydrocyanic acid passed through a red-hot porcelain tube, is partly resolved into cyanogen, hydrogen, and nitrogen gas [and charcoal?] (Gay-Lussac). — 2. Hydrocyanic acid vapour mixed with hydrogen is but imperfectly decomposed by a succession of electric sparks, the gaseous mixture depositing a small quantity of charcoal and increasing perceptibly in volume. (Gay-Lussac.) [This expansion is not very easy to account for, unless it be due to the formation of carbonic oxide or hydrogen arising from the presence of water.]—3. The liquid acid placed in the circuit of the voltaic battery yields hydrogen gas at the negative pole; no gas is set free at the positive pole, because, according to Gay-Lussac, the cyanogen there separated remains dissolved in the hydrocyanic acid, or, according to Davy, because cyanide of platinum is formed.

4. The anhydrous acid and its vapour, when set on fire by flaming bodies, burn in contact with air or oxygen gas, producing carbonic acid and nitrogen. According to Scheele, the vapour burns with a bluish red or yellow flame.—The vapour mixed with oxygen in the detonating eudiometer, explodes with great violence on the passage of an electric spark (Ittner), forming also a white cloud. In this reaction, a small quantity of nitric acid is produced as well as carbonic acid, water, and nitrogen. For complete combustion, $2\frac{1}{2}$ vol. oxygen are required to 2 vol. hydrocyanic vapour; after the explosion, $1\frac{1}{2}$ vol. gas (1 vol. hydrogen and $\frac{1}{2}$ vol. oxygen) are found to have disappeared, and there remain 2 vol. carbonic acid and 1 vol. nitrogen. (Gay-Lussac.)—Also when the vapour is passed over red-hot oxide of copper, there are formed 2 vol. carbonic acid and 1 vol. nitrogen, together with water. (Gay-Lussac.)

5. The anhydrous acid poured into a bottle filled with dry chlorine gas is converted in sunshine into hydrochloric acid and solid chloride of cyanogen:

$$3C^2NH + 6Cl = C^6N^3Cl^3 + 3HCl.$$

If the hydrocyanic acid is in excess, a yellow or red and more viscid mixture is produced, consisting of solid chloride of cyanogen and hydrocyanic acid.—If the chlorine is moist, decomposition takes place even in the dark, heat being evolved and a small quantity of solid chloride of cyanogen formed, together with carbonic acid, carbonic oxide, hydrochloric acid and ammonia.—Probably in this manner:

$$C^2NH + Cl + 3HO = CO + CO^2 + NH^4Cl.$$

If the vessel containing the hydrocyanic acid and moist chlorine be exposed to the sun, sal-ammoniac is formed, together with the yellow oil

which is produced by the action of moist chlorine upon cyanogen (p. 385), and regarded by Gay-Lussac as chloride of cyanogen. (Serullas, *Ann. Chim. Phys.* 35; 299; 38, 378.)—The action of chlorine upon dilute hydrocyanic acid produces carbonic acid, hydrochloric acid, and ammonia, which is decomposed by the further action of the chlorine. (Ittner; *comp.* Berthollet, *Ann. Chim.* 1, 35; *Statique chim.* 2, 263; Gay-Lussac, *Ann. Chim.* 95, 200; also *Schw.* 16, 55; also *Gilb.* 53, 168.)—*Iodine* or *phosphorus* volatilized in dry hydrocyanic acid vapour exerts no action. (Gay-Lussac.) According to Porrett, iodine with aqueous hydrocyanic acid forms hydriodic acid and cyanogen.—6. Aqueous hypochlorous acid with aqueous hydrocyanic acid forms chloride of cyanogen, cyanuric acid, hydrochloric acid, and free chlorine. (Balard.)—Nitric acid and hydrochloric acid [?] heated with anhydrous hydrocyanic acid to the boiling point of the latter, exert no action upon it. (Trautwein, *Repert.* 11, 15). Aqueous iodic acid likewise exerts no action, even with the aid of heat. (Millon.)

7. Moderately strong *Sulphuric* or *Hydrochloric* acid decomposes hydrocyanic acid, doubtless by its predisposing affinity for ammonia, into ammonia and formic acid, the elements of water taking part in the change (Pelouze):

$$C^2NH + 4HO = NH^3 + C\,H\,O^4.$$

A mixture of equal volumes of anhydrous hydrocyanic acid and fuming hydrochloric acid solidifies in five minutes, with rise of temperature, forming a crystalline mass, which, when distilled, yields first hydrocyanic, then hydrochloric, then formic acid, and leaves a residue of sal-ammoniac.—Sulphuric acid decomposes hydrocyanic acid more slowly; the mixture when distilled after a while yields formic acid; but if the sulphuric acid is in too large quantity or too concentrated, carbonic oxide (a product of the decomposition of formic acid by sulphuric acid) is given off.—With cyanide of potassium, also, excess of hydrochloric acid produces sal-ammoniac and formic acid, besides chloride of potassium. (Pelouze, *Ann. Chim. Phys.* 48, 395; also *J. Pharm.* 18, 172; also *Ann. Pharm.* 2, 84.)—Kuhlmann long ago remarked (*Ann. Chim. Phys.* 40, 441; also *Schw.* 56, 356; also *Pogg.* 16, 367) that a mixture of hydrochloric and anhydrous hydrocyanic acid deposits crystals of sal-ammoniac; and that oil of vitriol mixes with the product, producing rise of temperature, and though it does not deposit any crystals, gives off on the application of heat, first hydrocyanic acid, then a large quantity of combustible gas (carbonic oxide), and leaves a residue of sulphate of ammonia.—According to Trautwein, a mixture of oil of vitriol and anhydrous prussic acid becomes heated after a while, then intumesces strongly with a hissing noise and evolution of sulphurous acid [formic acid and carbonic oxide], and turns black.—Aqueous bisulphate of potash digested for a long time with hydrocyanic acid and evaporated, does not give rise to the formation of ammonia. (Gm.)

8. The same decomposition of hydrocyanic acid into formic acid and ammonia, is produced by the action of *fixed alkalis* at high temperatures, doubtless in consequence of their predisposing affinity for formic acid (Pelouze, and, likewise, Geiger, *Ann. Pharm.* 17, 44):

$$C^2NH + KO + 3HO = C^2NKO^4 + NH^3.$$

Cyanide of potassium, boiled in the state of concentrated aqueous solution, out of contact with the air, gives off ammonia, and is converted into

formiate of potash; the decomposition is rapid at first, but afterwards goes on slowly, so that, to decompose all the cyanide of potassium, it is necessary to boil for a long time, and with frequent renewal of the water. (Pelouze.) An excess of potash may possibly accelerate the decomposition. At ordinary temperatures, potash does not separate ammonia from hydrocyanic acid. (Gm.)

9. With *Peroxide of Lead*, aqueous hydrocyanic acid yields cyanide of lead, water, and cyanogen (Liebig, *Ann. Pharm.* 25, 3):

$$2HCy + PbO^2 = PbCy + 2HO + Cy.$$

Peroxide of Manganese completely absorbs hydrocyanic acid vapour mixed with hydrogen gas, but without separation of cyanogen. (Gay-Lussac.)—With *Cupric oxide*, hydrocyanic acid vapour mixed with hydrogen slowly produces, at ordinary temperatures, cyanogen gas and water. (Gay-Lussac.) [In this case, dicyanide of copper is probably formed:

$$2HCy + 2CuO = Cu^2Cy + 2HO + Cy.]$$

Certain *basic metallic oxides* act immediately on aqueous hydrocyanic acid, forming water and anhydrous metallic cyanides: *e.g.*, cuprous oxide and silver-oxide; others form solutions, which may be regarded either as hydrated metallic cyanides or as hydrocyanates of metallic oxides, some of which, however, are converted into anhydrous cyanides even in crystallizing; *e.g.*, mercuric oxide; others on evaporation to dryness; *e.g.*, potash. When vapour of anhydrous prussic acid is passed over strongly heated *Baryta*, the baryta becomes heated to dull redness, and fuses imperfectly, giving off, not water, but hydrogen gas; hydrate of potash gives off a larger quantity; *carbonate of soda* likewise evolves carbonic oxide gas. (Gay-Lussac.)—Gay-Lussac supposed that a compound of cyanogen with baryta, potash, or soda, was formed in this reaction; perhaps however there is formed a mixture of alkaline cyanate and metallic cyanide:

$$2C^2NH + 2BaO = C^2NBaO^2 + C^2NBa + 2H.$$

10. When hydrocyanic vapour is diffused through hydrogen or nitrogen gas to the amount of 2 vol., and potassium is heated in the mixture, cyanide of potassium is formed and 1 vol. hydrogen gas separated. (Gay-Lussac.)

11. Vapour of anhydrous prussic acid passed over fine iron wire heated to redness in a tube, yields nitrogen and hydrogen gases in equal volumes, and a brittle mass of iron, partly combined, partly coated with carbon. (Gay-Lussac.)

12. Hydrocyanic acid, even when kept in the dark in closely stoppered bottles which are quite filled with it, decomposes with various degrees of rapidity, becoming brown and viscid, and yielding hydrocyanate of ammonia and a brown solid substance (paracyanogen or azulmic acid?) (Ittner, Gay-Lussac.)—The more the acid is diluted with water or alcohol, the less is it liable to decomposition. Whether alcohol retards the decomposition more than water, and whether light accelerates it, are questions which require to be settled by direct experiment. Gay-Lussac's anhydrous prussic acid (p. 396) sometimes decomposes even in an hour, and never keeps longer than fourteen days. (Gay-Lussac.) Trautwein's anhydrous acid (p. 394) often keeps for a year (for several years, according to my experience) before decomposition begins; but the addition of a small quantity of potash or ammonia converts it in a few hours into a brownish black magma. (Trautwein, *Repert.* 12, 151.) Hydrocyanic

acid prepared according to Vauquelin's method (p. 396), by decomposing dry cyanide of mercury with dry sulphuretted hydrogen, may be kept unaltered for two months in the winter, either in the dark or exposed to light. (Cooper.)—The same hydrocyanic acid sometimes exhibits various degrees of permanency even under the same circumstances. A sample of Gay-Lussac's anhydrous acid was mixed with 3 times its volume of alcohol, and divided between two bottles, so that each should contain 3 drachms; and the bottles were covered with black paper, put into a wooden box, and kept for 8 years in a dark cellar. On being taken out, the liquid in one bottle was found to be transparent and colourless hydrocyanic acid, which had undergone no alteration; 4 drops of it killed a dog in a minute; but the liquid in the other bottle was turbid, had no taste or smell [not even that of the alcohol!] and half a tea-spoonful of it had no effect upon a dog. (Lalande, *J. Chim. méd.* 13, 228.)—Since, according to Trautwein's experience, alkalis accelerate the decomposition of hydrocyanic acid, it was natural to suppose (*Handb.* Aufl. 3, II., 467) that very small quantities of a stronger acid would retard it. This expectation appears to be confirmed by the following more recent observations: Hydrocyanic acid rectified over magnesia decomposes very quickly. (Schrader, *Berl. Jahrb.* 25, 1, 20; Kemmerich, *Br. Arch.* 12, 92.)—When hydrocyanic acid which is beginning to turn brown is distilled alone, the colourless distillate likewise turns brown very quickly; but if it be distilled over phosphoric acid, which retains the ammonia, the distillate is permanent; in general, any sample of hydrocyanic acid, either aqueous or alcoholic, may be rendered fit for keeping by distilling it over phosphoric acid. (Duflos, *Kastn. Arch.* 15, 219; also *Br. Arch.* 29, 65.)—Hydrocyanic acid containing hydrochloric acid keeps better than the pure acid. (Barry.) If hydrocyanic acid be distilled over lime, and 5 drops of hydrochloric acid be added to 2 oz. of the distillate, the acid so treated will keep, whereas the portion not mixed with hydrochloric acid soon turns brown. (Everitt.)—Perfectly pure hydrocyanic acid, even when mixed with water, soon turns brown; but a trace of sulphuric or hydrochloric acid prevents the decomposition. (Liebig, *Ann. Pharm.* 18, 70.)—Rectification over bases deprives hydrocyanic acid of any formic, sulphuric, or hydrochloric acid that it may contain,—substances which exert a protective action; but by rectification over phosphoric acid, any ammonia which may be present and would induce decomposition is withdrawn, and perhaps a volatile acid, such as formic acid, set free.—This spontaneous decomposition of hydrocyanic acid cannot be stoichiometrically developed till the composition of the brown substance produced in it shall have been ascertained. If this substance be actually paracyanogen $=C^6N^3$, or a hydrate of that body, other products must be formed beside hydrocyanate of ammonia; if on the contrary it be C^6N^3, the equation will be:

$$4C^2NH = C^6N^3 + NH^3,C^2NH.$$

Combinations of Hydrocyanic Acid.—a. With *Water.—Aqueous* or *Dilute Hydrocyanic acid.* Hydrocyanic acid mixes with water in all proportions. (Preparation, pp. 390–394).—The aqueous acid exhibits the same odour, taste, and poisonous action as the anhydrous acid, though in a lower degree. It freezes more readily, and is specifically heavier in proportion as it contains more water. According to Scheele and Ittner, it does not redden litmus; in reality, however, it does produce a slight reddening.

Per-centage of Anhydrous Hydrocyanic Acid in the Hydrated Acid, according to Ure (*Quart. J. of Sc.* 13, 321; also *Schw.* 36, 282).

Sp. gr.	Perc.	Sp. gr.	Perc.	Sp. gr.	Perc.	Sp. gr.	Perc.
0·9570	16·0	0·9900	5·8	0·9952	3·2	0·9974	2·0
0·9768	10·6	0·9914	5·3	0·9958	3·0	0·9975	1·77
0·9815	9·1	0·9923	5·0	0·9964	2·7	0·9978	1·7
0·9840	8·0	0·9930	4·6	0·9967	2·5	0·9979	1·6
0·9870	7·3	0·9940	4·0	0·9970	2·3		
0·9890	6·4	0·9945	3·6	0·9973	2·1		

According to Trautwein, aqueous hydrocyanic acid of sp. gr. 0·982 at 12·5° contains 10·53 per cent. of anhydrous acid.

b. With *Salifiable Bases;* vid. *Cyanides and Hydrocyanates.*

c. With *Metallic Chlorides.*

d. Hydrocyanic acid mixes with wood-spirit, alcohol, ether, volatile oils, and a few other liquid organic compounds.

Cyanides and Hydrocyanates or Prussiates.

Certain modes of formation of these compounds have already been given (pp. 379–383); the following, however, remain to be noticed. 1. Very few metals, potassium among the number, take up cyanogen and form cyanides, when heated in cyanogen gas or hydrocyanic acid vapour; in the latter case hydrogen is separated.—2. Cyanogen gas passed over certain heated alkalis and alkaline carbonates, drives out the carbonic acid, and forms a mixture of cyanide and cyanate; it acts in the same manner on the aqueous solutions of the fixed alkalis, excepting that a brown substance resembling paracyanogen is likewise formed.—3. With certain basic metallic oxides, as the oxide of silver, hydrocyanic acid immediately forms an anhydrous cyanide, with separation of water; but with most oxides it forms hydrated cyanides, which may be regarded as hydrocyanates of the oxides. To convert an aqueous alkali (which should be free from carbonic acid) completely into a metallic cyanide, hydrocyanic acid must be added to it, till it no longer forms a precipitate with sulphate of magnesia. (Ittner.)—4. The alkaline cyanates may be obtained in the hydrated state by treating cyanide of silver with the aqueous solution of the protosulphide of an alkali-metal. (Nimmo; F. & E. Rodgers.)

Cyanogen appears to have very little tendency to unite with the earth-metals.

Some cyanides are crystallizable. Some are colourless, others exhibit various colours. The cyanides of the alkali-metals in the state of aqueous solution, exhibit a strong alkaline reaction, and have a bitter and alkaline taste; the solution remains alkaline, even when mixed with a very large excess of hydrocyanic acid.

Hydrocyanate of ammonia or cyanide of ammonium volatilizes undecomposed when heated. The compounds of cyanogen with the alkali-metals sustain a red heat without decomposition, provided air and moisture be excluded. The cyanides of many of the heavy metals, *e.g.*, lead, iron, cobalt, nickel, copper, &c., under these circumstances, give off all their nitrogen in the form of gas, and are converted into a compound or mixture of 1 At. metal and 2 At. carbon; $C^2NM = C^2M + N$.—Cyanide of mercury is resolved into metallic mercury and cyanogen gas; and

cyanide of silver gives off half its cyanogen in the gaseous form, the other half, perhaps converted into paracyanogen, remaining combined with the silver. All cyanides, when heated in presence of water, are destroyed, those of the heavy metals generally giving off carbonic oxide, carbonic acid, hydrocyanic acid, and ammonia, and leaving the metal, together with a small quantity of charcoal. The cyanides of the alkali-metals are converted by continued boiling with water into ammoniacal gas and alkaline formiates. The cyanides of some of the alkali-metals, *e.g.*, cyanide of potassium, when heated in contact with the air, first take up 2 At. oxygen, and are converted into cyanates (C^2NKO^2), and these, when further heated, give off nitrogen and half the carbonic acid formed, and are converted into alkaline carbonates. The cyanides of the heavy metals take fire readily when heated, yielding nitrogen, carbonic acid, and metal or oxide. Cyanides detonate by percussion with chlorate of potash. (Johnston, *Schw.* 57, 379.)

Chlorine gas decomposes many cyanides, converting them into chlorides, and liberating cyanogen, chloride of cyanogen, either fixed or volatile, and a yellow oil, the products varying according to the presence or absence of light and water, the nature of the cyanide, and the proportion of chlorine present: *e.g.*,

$$HgCy + 2Cl = HgCl + CyCl.$$

Chlorine gradually introduced converts cyanide of lead or cyanide of silver into metallic chloride and free cyanogen, which does not take up any chlorine till all the cyanide is decomposed. (Liebig, *Pogg.* 15, 571.) Aqueous chloride of lime acts upon cyanide of silver with violent effervescence, evolving carbonic acid and nitrogen, together with a small quantity of cyanogen; but no cyanic acid is formed. (Liebig.) Iodine forms metallic iodide and cyanogen, or iodide of cyanogen. It decomposes the cyanides of the alkali-metals in the state of aqueous solution; also cyanide of silver or cyanide of copper dissolved in aqueous cyanide of potassium, forming a metallic iodide and liberating cyanogen. (Gerdy, *Compt. rend.* 16, 25; also *J. pr. Chem.* 29, 181.) With boiling aqueous cyanide of potassium, it forms iodide of potassium and iodide of cyanogen. (Liebig, *Ann. Pharm.* 50, 335.) It decomposes dry cyanide of mercury, forming iodide of mercury and iodide of cyanogen.

Strong nitric acid decomposes all metallic cyanides, with evolution of carbonic acid, nitrogen, &c. Excess of oil of vitriol decomposes metallic cyanides at high temperatures, forming a sulphate of the metallic oxide, sulphate of ammonia, and carbonic oxide. (Fownes.)

$$C^2NM + 4(HO,SO^3) = MO,2SO^3 + NH^3,HO^2SO^3 + 2CO.$$

Most cyanides, when treated with dilute acids, give off their cyanogen in the form of hydrocyanic acid:

$$KCy + HCl = KCl + HCy;$$

and,

$$KCy + HO,SO^3 = KO,SO^3 + HCl.$$

The cyanides of the alkali-metals, which, in the state of aqueous solution, may also be regarded as hydrocyanates, are decomposed by the weakest acids, even by carbonic acid (Scheele); hence their solution, if it does not contain excess of alkali, gives off hydrocyanic acid on exposure to the air, that acid being gradually expelled by the carbonic acid of the air. On the other hand, it is only the alkaline hydrosul-

phates and soap-solutions that are decomposed by hydrocyanic acid. (Scheele)

The compounds of cyanogen with the heavy metals are of a more intimate nature. Some, as the cyanides of zinc and lead, give off hydrocyanic acid when treated with dilute solutions of the stronger mineral acids, such as sulphuric acid; others, as the cyanides of mercury and silver, are not decomposed even by the strongest oxygen-acids, in the state of aqueous solution; but hydrogen-acids, such as hydrochloric and hydrosulphuric acid, decompose them; others again, as protocyanide of gold and protocyanide of iron, withstand the action of dilute sulphuric, hydrochloric, or nitric acid, even at a boiling heat.

From the solutions of the alkaline cyanides, many heavy metallic oxides separate part of the alkali-metal, in the form of oxide, which remains dissolved, forming at the same time a heavy metallic cyanide, or a compound of that cyanide with the cyanide of the alkali-metal:

$$KCy + HgO = HgCy + KO;$$

and,

$$2KCy + HgO = KCy,HgCy + KO.$$

All the cyanides of the alkali-metals are easily soluble in water; but among the cyanides of the heavy metals, there are but few which are soluble, *e.g.*, cyanide of mercury.

The cyanides of some metals form crystallizable compounds with the oxides of the same metal; with various metallic iodides, bromides, and chlorides; also with nitrates and chromates.

Cyanides have a strong tendency to unite with one another, and form definite compounds, called *Cyanogen-salts*, or *Double Cyanides*, (analogous to the iodine-, bromine-, and chlorine-salts,) which, in the hydrated state, may be regarded as *Double Hydrocyanates*. Thus crystallized cyanoplatinate of potassium, $KCy,PtCy^2 + 3Aq = KO,HCy + PtO^2,2HCy$.

Particularly numerous are the compounds of the alkaline cyanides (including cyanide of ammonium, NH^4Cy) with the cyanides of the heavy metals; they are formed and prepared as follows:

1. By saturating the aqueous solution of the cyanide of an alkali-metal with a heavy metallic cyanide, or if the latter be soluble in water, adding it to the alkaline cyanide in stoichiometrical proportion.—2. By saturating the aqueous solution of the alkaline cyanide with a heavy metallic oxide. In this case, part of the alkali-metal is separated in the form of oxide, which remains mixed with the solution, and the heavy metal passes over to the cyanogen-compound:

$$3KCy + FeO = 2KCy,FeCy + KO.$$

3. By digesting a heavy metallic cyanide with an aqueous alkali. In this case, on the contrary, part of the heavy metal is separated in the form of oxide:

$$3FeCy + 2KO = 2KCy,FeCy + FeO.$$

4. By fusing platinum with cyanide of potassium. The air in contact with the mixture converts the separated potassium into potash.—5. By adding aqueous hydrocyanic acid to a mixture, in equivalent proportions, of a heavy metallic oxide or its carbonate, and a caustic or carbonated alkali, till the acid retains its odour, even after long agitation at a gentle heat. In this case, the hydrocyanic acid drives out all the carbonic acid

that may be present, and the heavy metallic oxide is dissolved.—6. By saturating with caustic potash or carbonate of potash, the acid compound which hydrocyanic acid forms with certain heavy metallic cyanides.

The proportions in which the heavy metallic cyanides may thus be made to unite with the cyanide of an alkali-metal, *e. g.*, with cyanide of potassium, are the following:

a. 3 At. Cyanide of potassium to 1 At. Dicyanide of a heavy metal: $3KCy,Cu^2Cy$.

b. 1 At. Cyanide of potassium to 1 At. Dicyanide of a heavy metal: KCy,Cu^2Cy.

c. 2 At. Cyanide of potassium to 1 At. Protocyanide of a heavy metal: $2KCy,FeCy$;—$2KCy,IrCy$.

d. 1 At. Cyanide of potassium to 1 At. Protocyanide of a heavy metal: $KCy,ZnCy$;—$KCy,CdCy$;—$KCy,NiCy$;—$KCy,AgCy$;—$KCy,AuCy$; $KCy,PtCy$;—$KCy,PdCy$.

h. 1 At. Cyanide of potassium to 2 At. Protocyanide of a heavy metal: $KCy,2FeCy$.

f. 1 At. Cyanide of potassium to 1 At. Bicyanide of a heavy metal: $KCy,PtCy^2$.

g. 3 At. Cyanide of potassium to 1 At. Sesquicyanide of a heavy metal: $3KCy,Cr^2Cy^3$;—$3KCy,Mn^2Cy^3$;—$3KCy,Fe^2Cy^3$;—$3KCy,Co^2Cy^3$.

k. 1 At. Cyanide of potassium to 1 At. Tercyanide of a heavy metal: $KCy+AuCy^3$.

Almost all these compounds of an alkaline cyanide with a heavy metal, are crystallizable and soluble in water. Towards vegetable colours they are neutral or slightly alkaline, whereas the pure cyanides of the alkali-metals have a strong alkaline reaction; the double cyanides likewise emit little or no odour of hydrocyanic acid. They are also much less easily decomposible than the pure cyanides of the alkali-metals.

Both the metallic cyanides contained in these compounds behave, when ignited in a close vessel, just in the same manner as when they are ignited separately. Thus, in ferrocyanide of potassium, $2KCy,FeCy$, the cyanide of potassium remains undecomposed, while the cyanide of iron is resolved into nitrogen and carbide of iron.

With dilute solutions of the stronger oxygen-acids, they exhibit the following reactions. A few of them, as cyanide of zinc and potassium, $KCy,ZnCy$, are completely decomposed even by cold dilute sulphuric acid, yielding hydrocyanic acid and two sulphates. Others give off the hydrocyanic acid derived from the cyanide of potassium, forming an alkaline sulphate, whilst the heavy metallic cyanide either remains unaltered in the solution, as is the case with cyanide of mercury, or is precipitated alone, which is the case with cyanide of silver. A comparatively small quantity of hydrochloric acid may destroy the cyanide of the alkali-metal, and separate the heavy cyanide at first in the undecomposed state; but a larger quantity completely decomposes it, especially if aided by heat, into hydrocyanic acid and a chloride of the metal. Other double cyanides, *e. g.*, ferrocyanide of potassium, $2KCy,FeCy$, form indeed a potash-salt with cold sulphuric or hydrochloric acid; but the hydrocyanic acid, as it is set free, unites with the cyanide of the heavy metal, producing a peculiar soluble compound which reddens litmus, *e. g.*, $2HCy,FeCy$, and does not give off the hydrocyanic acid

till it is heated. Finally, some of these compounds withstand the action of dilute sulphuric or hydrochloric acid, even at a boiling heat.

Sulphuretted hydrogen precipitates the heavy metal, in the form of sulphide, from the dissolved compounds of the alkaline with the heavy cyanides, sometimes easily, as with cadmium, mercury, and silver, sometimes not at all, or but slowly and partially, as with zinc, iron, cobalt, nickel, and copper.

When the solution of such a compound of a cyanide of an alkali-metal with the cyanide of a heavy metal, is mixed with the salts of other heavy metals, precipitates are formed, exhibiting strong and varied colours, and generally consisting of compounds of the heavy cyanide already present with another heavy cyanide, formed by double decomposition between the cyanide of the alkali-metal and the salt of the heavy metal which has been added. Thus, ferrocyanide of potassium forms with sulphate of copper a red precipitate of ferrocyanide of copper:

$$2KCy,FeCy + 2(CuO,SO^3) = 2CuCy,FeCy + 2(KO,SO^3).$$

But these precipitates often retain part of the original cyanogen salt in a state of intimate combination, so that in many cases it cannot be completely extracted even by boiling water.

The cyanides and double cyanides, which have just been discussed in a general manner, must, as first proposed by Graham (*Lehrb.*), be divided into classes, according to their peculiar properties.

1. The *true cyanides*, which include the greater number, exhibit the poisonous action of hydrocyanic acid. They are decomposed by the stronger acids, at least by hydrochloric acid, even at ordinary temperatures. The compounds of heavy metallic cyanides of this class with the cyanides of the alkali-metals, generally exhibit a slight alkaline reaction. Dilute acids separate hydrocyanic acid, even in the cold, from the cyanide of the alkali-metal contained in them, precipitate the heavy cyanide if it be insoluble, and then, in most cases, exert a decomposing action upon it.

2. Other cyanides, among which we must not only reckon, as Graham does, the iron-compounds, but likewise those of chromium, cobalt, and perhaps also manganese, do not exhibit the poisonous action of hydrocyanic acid, either alone or in combination with cyanide of potassium. Their compounds with cyanide of potassium are perfectly neutral. The strongest acids, at ordinary temperatures, do not liberate hydrocyanic from these compounds, but convert them into a potash-salt and a kind of metallo-hydrocyanic acid, which reddens litmus strongly, is not poisonous, and is resolved by heat into hydrocyanic acid and a metallic cyanide. Thus ferrocyanide of potassium with hydrochloric acid yields chloride of potassium and hydroferrocyanic acid:

$$2KCy,FeCy + 2HCl = 2HCy,FeCy + 2KCl;$$

or,

$$C^6N^3FeK^2 + 2HCl = C^6N^3FeH^2 + 2KCl.$$

All compounds of heavy metallic cyanides of this class, with cyanide of potassium and other cyanides, contain 3 or 2 . 3, or 3 . 3 At. cyanogen. Hence Graham supposes, with some probability, that the constituents of 3 At. cygnogen, C^2N, are united into a single atom, C^6N^3, which combination he designates by the term *Prussian*, so that these compounds may be called *Prussides*.

There are likewise other cases in which we are compelled to suppose that the 6 At. carbon and 3 At. nitrogen unite into a single compound atom. Thus the brown paracyanogen, which remains after the ignition of cyanide of mercury, is supposed to be C^6N^3, and according to that supposition would be identical with *Prussian*. Cyanuric acid, $C^6N^3H^3O^6$, which is polymeric with cyanic acid, C^2NHO^2, and solid chloride of cyanogen, $C^6N^3Cl^3$, which is polymeric with gaseous chloride of cyanogen, C^2NCl, are formed from cyanogen and its compounds, and under certain circumstances are again resolved into the latter. According to this view, certain metals, such as iron, appear to possess the power of transforming 3 At. of cyanogen, C^2N, into 1 At. of paracyanogen or prussian.

Regarding these compounds from the point of view of the nucleus-theory, we must suppose that the primary nucleus, C^6H^6, yields the secondary nuclei, $C^6N^3H^3$, $C^6N^3Cl^3$, $C^6N^3Fe^3$, $C^6N^3FeH^2$, $C^6N^3FeK^2$, &c. The first, which is not known in the separate state, forms with 6O, cyanuric acid, $C^6N^3H^3O^6$. It is composed of 3 square tables of hydrocyanic acid, placed one upon the other in the form of a square prism, probably in such a manner that the two carbon-atoms of the middle table come in contact above and below with H- and N-atoms. In $C^6N^3FeH^3$, the H-atom of the middle table is replaced by an Fe-atom, and in $C^6N^3Fe^3$, all the 3 H-atoms are replaced by 3 Fe-atoms. In $C^6N^3Fe^2$, however, the nucleus exhibits a vacant space, unless we suppose, as Laurent does, that this compound contains 3 At. iron, each of which weighs $\frac{2}{3}$ as much as an ordinary iron-atom.

¶ Adopting Gerhardt's equivalents (p. 27,) and admitting that the two classes of iron-compounds, *i.e.*, the ferrous and ferric salts, contain different metals, viz., *ferrosum* = Fe = 28, and *ferricum* = $f = \frac{2}{3}$ of 28,—and similarly with platinum (VI., 313), *platinosum* = Pt = 99, *platinicum* = pt = 49·5,—the formulæ of the ferrocyanides, ferridcyanides, cobaltocyanides, &c., may all be reduced to the general expression $C^2N^2M^2$, in which M denotes the sum of the equivalents of two or three different metals; thus:

Ferrocyanides = $C^2N^2Fe^{\frac{1}{2}}M^{\frac{1}{2}}$.
Ferrocyanide of Potassium = $C^2N^2Fe^{\frac{1}{2}}K^{\frac{1}{2}} + 2HO$.
Ferrocyanide of Potassium and Barium = $C^2N^2Fe^{\frac{1}{2}}K^{\frac{1}{2}}Ba^{\frac{1}{2}} + 2HO$.
Prussian blue = $C^2N^2Fe^{\frac{1}{2}}f^{\frac{1}{2}} + 2HO$.
Ferridcyanides = C^2N^2fM.
Cobaltocyanides = C^2N^2CoM.
Platinocyanides = C^2N^2PtM.
Platino-platinidcyanides = $C^2N^2Pt^{\frac{2}{3}}pt^{\frac{1}{3}}M^{\frac{1}{2}}$.

(Laurent, *Compt. rend.* 26, 294; *Pharm. Centr.* 1848, 23; *J. pr. Chem.* 42, 128; *Jahresber.* 1847–8, 484.) ¶.

If the secondary nucleus $C^6N^3H^3$ be denoted by a particular name—*Prusse*, for example—then, according to the nomenclature given on pages 149–152, $C^6N^3Fe^3$ = *Prussemirt*; $C^6N^3H^2Fe$ = *Prussemart*; $C^6N^3K^2Fe$ = *Prussepetemart*, &c.—$C^6N^3Fe^2$ will be *Prussümert*, because ü = 0, and therefore expresses in this case that 1 At. of the deficient hydrogen is not replaced by iron. According to this mode of designation ($C^6N^3K^2$,$C^6N^3Fe^2$) = *Prussümert-Prussepit*.

¶ According to Schrötter (*Wien. Acad. Ber.* 1249, Mar. 316; *Jahresber.* 1849, 211) the double cyanides may all be reduced to the types nMCy and M^5Cy^6, where M denotes an equivalent of metal, and *n* the numbers 1, 2, 3, and 11; nM, or 5M may be represented by several metals, and in the cyanides 2MCy and 3MCy, part of the cyanogen may be replaced by O, I, Br or Cl. Thus the form nMCy includes the compounds KCy, $KZnCy^3$, K^3FeCy^3, and $M^6Pt^5Cy^{11}$ (the salts lately discovered

by Quadrat.) The type M^4Cy^6, includes ferridcyanide of potassium, $K^3Fe^2Cy^6$, and the corresponding salts. ¶

CYANIDE OF AMMONIUM OR HYDROCYANATE OF AMMONIA.—$NH^4Cy = NH^3,HCy = C^2N(NH^4)$. For some of the modes of formation, *vid.* pp. 381–383.—1 vol. ammoniacal gas unites with 1 vol. hydrocyanic vapour, forming 2 vol. vapour of cyanide of ammonium.

Preparation of the dry salt. 1. By heating the following substances, which must be as dry as possible, in a distillatory apparatus, the receiver of which is surrounded with ice and salt: either the compound of cyanide of iron with cyanide of ammonium, or a mixture of cyanide of potassium and sal-ammoniac (Berzelius), for which the heat of the water-bath is more than sufficient (Berzelius, *Lehrb.*); or an intimate mixture of 3 pts. ferrocyanide of potassium and 2 pts. sal-ammoniac (Bineau):

$$2KCy,FeCy + 2NH^4Cl = 2NH^4Cy + 2KCl + FeCy;$$

or an intimate mixture of 126 pts. (1 At.) cyanide of mercury and 54 pts. (1 At.) sal-ammoniac (Bineau, *Ann. Chim. Phys.* 67, 231):

$$HgCy + NH^4Cl = NH^4Cy + HgCl.$$

This mixture fuses at a gentle heat, giving off vapours of hydrocyanate of ammonia, and leaving corrosive sublimate. (Bineau.)

2. By passing dry ammoniacal gas through dry charcoal heated to redness in a porcelain tube, and thence into a U-tube surrounded with a freezing mixture, in which the compound condenses in small prisms. (Langlois, *Ann. Chim. Phys.* 67, 111.)

Crystallizes in colourless cubes or in fern-like tufts (Gay-Lussac); in anhydrous square prisms. (Berzelius.) Boiling point about + 36°. Tension of vapour at + 22° = 0·45 met. (Gay-Lussac.) Has an alkaline reaction. Smells and tastes of ammonia and hydrocyanic acid together (Ittner); highly poisonous. (Langlois.)

				Or:				
NH^3	17	38·64		NH^4	18	40·91		
HCy	27	61·36		Cy	26	99·09		61·54
NH^4Cy	44	100·00			44	100·00		
Ammoniacal gas					1	0·5893		
Hydrocyanic acid vapour					1	0·9359		
Cyanide of Ammonium vapour					2	1·5252		
					1	0·7626		

The vapour easily takes fire and burns with a yellowish flame (Bineau), depositing carbonate of ammonia. (Ittner.) The crystals remain undecomposed for some time, if kept in a closed vessel surrounded with ice; but at ordinary temperatures they decompose, the decomposition being more rapid as the temperature is higher (Langlois); on the direct application of heat, it takes place very quickly. (Gay-Lussac.) In hydrogen gas, it is somewhat slower than in air from which it can absorb oxygen, (Bineau.) The crystals in decomposing retain their form, but are converted into a black-brown substance, azulmic acid. (Berzelius.) Chlorine decomposes the salt, with evolution of heat and formation of volatile chloride of cyanogen; bromine acts in a similar manner. (Langlois.)

The salt dissolves in water and in alcohol. The aqueous solution

may also be obtained by mixing aqueous hydrocyanic acid with aqueous ammonia, or by distilling 2 pts. of ferrocyanide of potassium with 3 pts. sal-ammoniac and 10 pts. water (Ittner), or by distilling an aqueous solution of 127 pts. (1 At.) cyanide of mercury and 54 pts. (1 At.) sal-ammoniac. (Duflos, *Schw.* 65, 106.)

CYANIDE OF POTASSIUM.—$KCy=C^2NK$.—Various modes of formation have already been given (pp. 379–383). Cold potassium absorbs but a small quantity of cyanogen gas, because it becomes covered with a crust; but the metal, when heated, absorbs as many volumes of the gas as it would evolve of hydrogen from water, and is converted into yellowish cyanide of potassium; when heated in hydrocyanic acid vapour, it takes the cyanogen from a volume of the vapour twice as great, liberating 1 vol. hydrogen, and is itself converted into grey spongy cyanide of potassium which fuses to a yellow mass when heated. (Gay-Lussac.) Hydrocyanic acid evolves sulphuretted hydrogen from aqueous monosulphide of potassium.

Preparation. 1. By mixing strong hydrocyanic acid with a strong aqueous or alcoholic solution of potash. Wittstein (*Repert.* 65, 364) mixes strong aqueous hydrocyanic acid in equivalent proportion with strong aqueous potash free from carbonic acid, the strength of both liquids having been previously determined.—Brande and Wiggers (*Ann. Pharm.* 29, 65) distil 2 pts. of ferrocyanide of potassium with 1½ pts. oil of vitriol and 4 pts. of water till the mass begins to jump, and pass the vapour into a cooled receiver containing the filtered solution of 1 pt. of hydrate of potash (not fused, but evaporated till it solidifies on cooling) in 3 or 4 pts. of alcohol of 90 per cent. or stronger. The cyanide of potassium, as it forms, falls to the bottom from the beginning of the action, and the contents of the receiver ultimately form a solid magma. The solid product is drained as completely as possible on a filter, the crystals washed several times with strong alcohol, then well pressed between bibulous paper, and dried as quickly as possible, *e.g.*, on a heated iron plate. In this manner, 8 parts of ferrocyanide of potassium yield 3 parts of cyanide in the form of a white crystalline powder. For the success of this process, it is important that the hydrocyanic acid be as strong as possible, so that a weak acid must first be dehydrated by chloride of calcium; that the strength of the alcohol be at least 92 per cent.; and that the solution of the potash in that liquid be fresh, inasmuch as it turns brown after a while. When the hydrocyanic acid is in excess, the cyanide of potassium appears to remain dissolved in the liquid for a longer time; hence the potash-solution must be in slight excess. (Herberger, *Repert.* 71, 122.)

2. An aqueous solution of cyanide of mercury is precipitated by aqueous solution of monosulphide of potassium in equivalent proportion, and the sulphide of mercury separated by filtration. (F. & E. Rodgers, *Phil. Mag. J.* 4, 93.)

3. Ferrocyanide of potassium perfectly deprived of its water, is gently ignited, out of contact of air, in vessels of cast or wrought iron, till no more nitrogen goes off, and the cyanide of potassium is separated from the admixed carbide of iron by solution in water or alcohol:

$$2C^2NK,C^2NFe = 2C^2NK + FeC^2 + N.$$

If too strong a heat be applied, the cyanide of potassium is resolved into

nitrogen gas and carbide of potassium, so that the residual mass evolves hydrogen in contact with water. (Berzelius, *Lehrb.*)

Clark (*J. Chim. méd.* 7, 544) coarsely breaks up the crystallized ferrocyanide of potassium; partially dehydrates it by heat, and then pulverizes it more finely; afterwards heats it in an open vessel till it has lost all its water and is converted into a white powder; introduces this powder into a wrought-iron bottle connected with a bent iron tube passing under water [a cast-iron bottle with a straight tube connected by means of a cork with a glass gas-delivery tube may likewise be used]; ignites the mass strongly as long as nitrogen continues to be evolved from it (or till a sample taken out with a curved wire appears pure white, and when dissolved in water, forms with hydrochlorate of ferric oxide, which must be quite free from ferrous oxide, a brown precipitate which dissolves in hydrochloric acid without leaving a residue of prussian blue); dissolves the residue in water; filters to separate the carbide of iron; evaporates; cools the solution to the crystallizing point; and proceeds in the same manner with the rest of the liquid as long as crystals can be obtained from it. The crystals are dried at a moderate heat, and preserved in well-closed bottles. If the decomposition is not complete, the ferrocyanide of potassium crystallizes out first.

Chevallier (*J. Chim. méd.* 6, 758) exhausts the ignited mass with absolute [?] alcohol, and separates the alcohol from the filtrate by distillation.

Robiquet (*J. Pharm.* 17, 643) keeps the resulting mixture of cyanide of potassium and carbide of iron in a state of fusion for some time [in a well-covered crucible it is to be supposed]; so that the carbide of iron may settle down, and the white mass at the top may be mechanically separated after cooling. It is not so good a plan to dissolve the mixture in a small quantity of water, evaporate the filtrate immediately to dryness, and heat the residue till it fuses, because ammonia and formiate of potash may be thereby formed. The decomposition does not, however, take place so quickly as Tilloy supposes, especially if, as Berzelius recommends, the filtrate be evaporated in vacuo over oil of vitriol. If the ferrocyanide of potassium contains sulphate of potash, it must be previously freed from that impurity by recrystallization. (Schindler, *Mag. Pharm.* 36, 67.)

On the surface of the mass thus decomposed by ignition and slowly cooled, are found splendid pure crystals which may be loosened with the spatula. The rest of the mass is finely pounded, and quickly exhausted with cold water, because if the liquid were heated, the iron which has been separated would re-dissolve in the cyanide of potassium [with evolution of hydrogen and formation of potash], and reproduce ferrocyanide of potassium; after which the filtrate is evaporated in a retort, and cooled till it crystallizes. The mother-liquid, besides cyanide of potassium left in solution, contains formiate of potash, caustic potash, and a small quantity of carbonate of potash (if it be evaporated in an open vessel, less formiate and more carbonate are produced). (Geiger, *Ann. Pharm.* 1, 44.)

The ignited mass is pulverized, placed upon a glass funnel, exhausted with cold water, and the stronger ley which is first obtained, evaporated quickly to dryness; or it is well boiled with 60 per cent. alcohol, which deposits the greater part of the cyanide of potassium on cooling. (Liebig, *Chim. org.* 1, 147.) The cyanide of potassium obtained by this process is not free from ferrocyanide, unless it be mechanically separated from carbide of iron before treating it with alcohol and water; for when the

mass is digested in water, the iron recombines with the cyanide of potassium. (Wittstein.)

4. For many purposes Wöhler's method (p. 395) is well adapted; the resulting preparation contains carbonate of potash, charcoal, and iron.

5. A mixture of 2 At. (184 pts.) of dry ferrocyanide of potassium with 2 At. (69 pts.) carbonate of potash is fused at a gentle heat in a covered porcelain crucible, and the product, which contains 5 At. cyanide of potassium and 1 At. cyanate of potash, is poured off from the separated iron, or exhausted after cooling with water or alcohol (F. & E. Rodgers, *Phil. Mag. J.* 1834, 4, 93):

$$2(2KCy,FeCy) + 2(KO,CO^2) = 5KCy + KO,CyO + 2CO^2 + 2Fe.$$

Strictly speaking, however, the quantity of cyanate of potash formed is somewhat greater; for the ferrous carbonate formed at the beginning of the action is resolved in the same manner as when heated alone, into carbonic acid, carbonic oxide, and ferroso-ferric oxide, which, when subsequently reduced to the metallic state, forms an additional quantity of cyanate of potash, larger in proportion to the excess of oxygen in this oxide over that in the protoxide. (Liebig.)

Liebig (*Ann. Pharm.* 41, 285) mixes intimately 8 pts. of ferrocyanide of potassium, dehydrated by heating it on an iron plate till it is slightly roasted, with 3 pts. of pure, dry carbonate of potash; throws the mass into a crucible at a low red heat; ignites it very gently, till samples of the fused mixture, taken out from time to time with a glass rod, no longer solidify to a brown or yellow, but to a white mass; then takes the crucible out of the fire; stirs the mixture several times with the glass rod; and, after leaving it for some time to enable the heavier portion to subside, pours the transparent and colourless liquid from the grey spongy mass into a hot porcelain dish. The residue in the crucible may still be rendered available by exhausting it with cold water, and heating the solution with sulphide of iron; ferrocyanide of potassium is then reproduced, and after it has crystallized out, sulphide of potassium remains in the mother-liquid.

The carbonate of potash used in this preparation must be quite free from sulphate, which would be reduced by the cyanide of potassium to the state of sulphide of potassium. An iron crucible is preferable to the earthen one, because the latter is penetrated by the mass, and imparts silicate of potash to it. A dull red heat must be uniformly maintained during the whole process. The cyanide of potassium thus obtained, forms a white mass free from granules of iron. Its aqueous solution should be transparent and colourless. (Haidlen & Fresenius, *Ann. Pharm.* 43, 130.) The ignition must not be continued till the evolution of gas ceases, otherwise the cyanide of potassium obtained will be grey; but the crucible must be removed from the fire, as soon as an extracted sample appears white after cooling; moreover, the deposition of the iron should be favoured by a few slight blows upon the crucible; the cyanide of potassium poured, through a fine sieve previously heated, into a vessel of silver, iron, or porcelain, having smooth sides; and the upper mass, which is pure, separated, after slow cooling, from the lower portion by means of a sharp instrument. (Clemm, *Ann. Pharm.* 61, 250.)

If the two salts are not quite dry, or not mixed in exactly equivalent proportions, a large quantity of ammonia is evolved during the fusion. (Glassford & Napier, *Phil. Mag. J.* 25, 58.)

If the mass [containing iron] be exhausted with water, or even with

alcohol, the solution will contain more or less ferrocyanide of potassium. (Wittstein, *Repert.* 65, 364.)

6. A mixture of 13 pts. carbonate of potash and 10 pts. prussian blue is ignited in a covered crucible, and the mass, after cooling, exhausted with water or alcohol. Or cyanide of mercury is thrown upon carbonate of potash heated nearly to redness. (F. & E. Rodgers.)

7. Cyanide of potassium is obtained in an impure state and on the large scale by igniting in cast-iron vessels a mixture of carbonate of potash with an equal or a double quantity of azotized organic matters, such as dried blood, flesh, horn, or skins, or with the azotized charcoal which remains after subjecting the above-named substances to dry distillation. The potassium hereby reduced from the carbonate of potash by the action of a portion of the charcoal, combines with another part of the charcoal and with nitrogen of the animal substance, forming cyanide of potassium. When this mass is exhausted with water, there remains a charcoal, distinguished by great decolorizing power, and a colourless or yellowish solution of cyanide of potassium is obtained, contaminated, however, with carbonate, phosphate, and sulphate of potash, sulphide, chloride, ferrocyanide, and sulphocyanide of potassium, or at all events with some of these bodies. By evaporating this solution till it half solidifies, and exhausting with alcohol, a somewhat purer cyanide of potassium is exhausted.

¶ 8. Cyanide of potassium is also prepared on the large scale by passing nitrogen gas over an intensely ignited mixture of charcoal and potash (p. 380). A vertical shaft, the middle portion of which is inclosed within the flue of an adjoining furnace, is filled with fragments of charcoal saturated with potash. The charcoal thus becomes intensely heated, and likewise receives a supply of nitrogen from the furnace through a number of small openings communicating with the outer flue. The materials are filled in at the top of the shaft, through which they gradually descend, and ultimately fall into a pan of water at the bottom, where the cyanide of potassium is dissolved. This process is conducted on an extensive scale at Newcastle. (*Vid.* Bramwell, *Repertory of Inventions*, 9, 280; also *Graham's Elements of Chemistry*, 2nd Ed. 1, 387, 388, where a figure of the arrangement is given.) ¶

Impurities. 1. *Carbonate of Potash.* Remains behind when the cyanide is dissolved in hot alcohol of 36° Bm., exhibiting its alkaline reaction, effervescence with acids, &c. On agitating the impure cyanide with cold alcohol of 78 per cent., the carbonate of potash deliquesces, and forms a fluid layer at the bottom. (Geiger.)—2. *Sulphide of Potassium.* The salt forms a dirty precipitate with lead-salts, instead of a white one; the gas which rises on the addition of an excess of dilute sulphuric acid imparts a brown colour to paper moistened with acetate of lead.—3. *Sulphate of Potash.* Precipitate with baryta-salts, after supersaturation with hydrochloric acid.—4. *Chloride of Potassium.* The salt ignited with twice its weight of nitre and 10 times its weight of carbonate of potash (which should both be free from chlorine), then dissolved in water, and supersaturated with nitric acid, precipitates nitrate of silver.—5. *Silicate of Potash.* Residue of silver, after supersaturation with hydrochloric acid, evaporation to dryness, and re-solution in water.—6. *Ferrocyanide of Potassium.* The solution mixed with a small quantity of ferric salt (which should be quite free from ferrous salt), and then with hydrochloric acid, yields prussian blue; with sulphate of copper, the solution gives a precipitate which, on the addition of dilute hydrochloric

acid, does not turn white but reddish.—7. *Sulphocyanide of Potassium.* The solution, supersaturated with hydrochloric acid, turns ferric salts yellowish red.—8. *Cyanate of Potash.* The hot solution of cyanide of potassium prepared by Rodgers's process, yields laminæ of cyanate on cooling. If that portion of the cyanide of potassium which is soluble in alcohol of 36° Bm., gives off carbonic acid on the addition of acids, and precipitates carbonate of baryta from baryta-salts, the presence of cyanate of potash may be inferred; it is possible, however, that a small quantity of carbonate of potash may be dissolved by the spirit. —10. *Formiate of Potash.*—*a.* The cyanide of potassium blackens on ignition.—*b.* On passing carbonic acid gas through the aqueous solution till all the hydrocyanic acid is expelled, exhausting the evaporated mass with alcohol, evaporating to dryness, and distilling the dry residue with dilute sulphuric acid, the formic acid distils over, and may be recognized by its power of reducing mercury and silver-salts (p. 275).

Lastly, the value of cyanide of potassium may be tested by Glassford & Napier's method, viz., by determining the quantity of pure cyanide contained in it. For this purpose, it is necessary to ascertain the exact quantity of the solution of cyanide of potassium under examination, required to redissolve the precipitate of cyanide of silver which is formed on first adding that solution to a given quantity of nitrate of silver solution of known strength. Since 1 At. cyanide of potassium is required to precipitate 1 At. silver, and 1 At. cyanide of potassium more to redissolve the precipitate as cyanide of silver and potassium, it follows that 1 At. silver precipitated and redissolved indicates the presence of 2 At. cyanide of potassium. If, therefore, the silver-solution used contains 108 pts. of silver, the quantity of cyanide of potassium thereby indicated is $2 . 65{\cdot}2 = 130{\cdot}4$. Liebig's method (p. 397) may also be used for testing the value of commercial cyanide of potassium.—*Vid.* also Fordos & Gélis (*Compt. rend.* 35, 224).

Properties. Crystallizes in transparent and colourless cubes after fusion, and in anhydrous octohedrons and cubo-octohedrons from its aqueous solution. At a dull red heat, it fuses into a transparent and colourless liquid, the crystals obtained in the moist way decrepitating slightly when thus treated. (Geiger.) At a white heat, it appears to volatilize undecomposed. Inodorous (in the moist state, however, it smells of hydrocyanic acid, from the action of carbonic acid in the air). Tastes strongly alkaline and bitter, like hydrocyanic acid. Has a strong alkaline reaction. Highly poisonous.

	Calculation.		
2 C	12·0		18·41
N	14·0		21·47
K	39·2		60·12
C^2NK	65·2		100·00

The aqueous solution may be kept unaltered in closed vessels at ordinary temperatures; but when boiled, it is resolved into ammoniacal gas and formiate of potash (Pelouze, *Ann. Chim. Phys.* 48, 398; Geiger, *Ann. Pharm.* 1, 54):

$$C^2NK + 4HO = C^2HKO^4 + NH^3.$$

The decomposition takes place rapidly at first, but slowly afterwards, so that to decompose all the cyanide of potassium, it is necessary to renew the water frequently. Cyanide of potassium heated with hydrate of potash likewise yields ammoniacal gas and formiate of potash at first;

but the latter compound is resolved, before the heat rises to redness, into hydrogen and carbonate of potash. (Pelouze.)—Hence, as Gay-Lussac long ago observed (*Ann. Chim. Phys.* 8, 440), ammonia is likewise evolved, when hot cyanide of potassium is dissolved in water, or cold cyanide of potassium in hot water.

When the solution is boiled down in contact with the air, a greater quantity of hydrocyanic acid is evolved, and there remains more carbonate than formiate of potash. (Geiger.) When moist or dissolved cyanide of potassium is exposed to the air at ordinary temperatures, it gradually absorbs carbonic acid, gives off hydrocyanic acid, and is converted into carbonate.

Cyanide of potassium detonates violently when heated with nitrate or chlorate of potash.

Cyanide of potassium under various circumstances takes up 2 At. oxygen, and is thereby converted into cyanate of potash. This effect takes place, though very slowly, when the cyanide is fused in contact with the air; more quickly when it is fused with peroxide of manganese, arsenious acid, antimonic oxide, antimonious acid, stannic oxide, lead-oxide, ferroso-ferric and ferric oxide, and cupric oxide (with visible combustion). The peroxide of manganese is thereby reduced to protoxide, and the other oxides to the metallic state. (Liebig, *Ann. Pharm.* 41, 289.) —Cyanide of potassium fused with sulphate of potash yields cyanate of potash and sulphide of potassium (Liebig, *Ann. Pharm.* 38, 31):

$$KO,SO^3 + 2KCy = KS + 2KCyO^2.$$

[If the mixture be fused at a gentle heat only, the decomposition is very imperfect.]—Cyanide of potassium may likewise exert a reducing action in the moist way; thus, from aqueous alloxan, after a few hours, it throws down dialurate of potash. (Liebig.)

Cyanide of potassium fused with sulphur is converted into sulphocyanide (Porrett), and similarly when heated with sulphide of antimony or sulphide of tin, the fused metal separating out. (Liebig.)—Sulphur does not dissolve in aqueous cyanide of potassium; but selenium dissolves readily, even at ordinary temperatures. (Wiggers, *Ann. Pharm.* 29, 319.)

Cyanide of potassium boiled with iodine takes up a large quantity of that substance, forming first a brown and afterwards a colourless liquid, which solidifies on cooling, and forms a crystalline magma of iodide of cyanogen. (Liebig, *Ann. Pharm.* 50, 355.) Probably in this manner:

$$KCy + 2I = KI + CyI.$$

It takes up iodide of nitrogen without any evolution of gas; the colourless solution evaporated in vacuo, yields a crystallo-granular, very deliquescent mass, the solution of which smells of iodoform, and produces a yellow precipitate with corrosive sublimate. (Millon, *Ann. Chim. Phys.* 69, 78.)

Cyanide of potassium deliquesces in the air and dissolves very abundantly in water. The same solution may be obtained by adding hydrocyanic acid to aqueous solution of potash till the liquid no longer gives a precipitate with neutral hydrochlorate of magnesia. (Ittner.)

Cyanide of potassium is almost insoluble in absolute alcohol; it dissolves in 80 pts. of boiling spirit of 95 per cent.; somewhat more readily in 78 per cent., and abundantly in 35 per cent. spirit; from its aqueous solution it is precipitated by spirit of 95 per cent. (Geiger.)

Aqueous cyanide of potassium dissolves several of the heavy metals, forming potash and a compound of the undecomposed cyanide of potas-

sium with the new cyanide. Zinc, iron, nickel, and copper, it dissolves, with evolution of hydrogen, even when not in contact with the air; but cadmium, silver, and gold are dissolved by it only when the air has access, its oxygen then combining with part of the potassium. On tin, mercury, and platinum it exerts no action (Elsner, *J. pr. Chem.* 37, 441):

$$2KCy + Zn + HO = KCy,ZnCy + H + KO;$$

$$2KCy + Cd + O = KCy,CdCy + KO.$$

For older statements respecting cyanide of potassium, *vid.* Richter (*über die N. Gegenst. d. Chem.* 11, 46); Bucholz (*A. Gehl.* 1, 406); Proust (*N. Gehl.* 3, 549); Ittner (*in his work on Hydrocyanic acid*, p. 35).

CYANIDE OF SODIUM.—C^2NNa.—May be obtained like cyanide of potassium by processes similar to 2, 3, 5, and 6, excepting that if process 5 be used, the heat must be raised somewhat above low redness, and in process 6 only 10 parts of dry carbonate of soda must be used to 10 pts. of prussian blue. The ignited mass is exhausted with boiling alcohol, from which the cyanide of sodium crystallizes. (F. & E. Rodgers, *Phil. Mag. J.* 4, 94.) When the aqueous solution of this salt, which may be formed by mixing aqueous soda with hydrocyanic acid, is evaporated, it first yields crystals and then coagulates to a saline mass. (Ittner.)

CYANIDE OF BARIUM.—$BaCy=C^2NBa$.—May be obtained in the dry state by igniting ferrocyanide of barium in a close vessel (Berzelius, *Lehrb.*); and in the state of aqueous solution by adding hydrocyanic acid to baryta-water, till it no longer precipitates neutral hydrochlorate of magnesia. (Ittner.) The solution has an alkaline reaction; is decomposed by carbonic acid (Scheele), and when boiled gives off ammonia and carbonic acid [?], at the same time depositing carbonate of baryta, and small tables of hydrocyanate [formiate] of baryta. (Ittner.)—Cyanide of barium dissolves readily in water, and with tolerable facility also in rectified spirit. (F. & E. Rodgers.)

CYANIDE OF CALCIUM. Obtained in the form of aqueous solution, or as hydrocyanate of lime, by saturating aqueous hydrocyanic acid with hydrate of lime and filtering.—Scheele precipitates the excess of lime taken up by the water, by adding an equivalent quantity of aqueous carbonic acid; Ittner & Schindler, on the other hand (*Mag. Pharm.* 36, 67), add hydrocyanic acid to the filtrate till it no longer precipitates a neutral solution of hydrochlorate or sulphate of magnesia.—Carbonic acid added to a solution of cyanide of calcium throws down the lime. (Scheele.) When it is distilled, all the hydrocyanic acid passes over, leaving the lime behind (Scheele); when boiled, it gives off hydrocyanic and carbonic acid, and leaves carbonate of lime. (Ittner.)

CYANIDE OF MAGNESIUM: aqueous.—Recently precipitated hydrate of magnesia dissolves readily in aqueous hydrocyanic acid; calcined magnesia dissolves slowly. The solution is decomposed by the carbonic acid of the air, just like potash-ley or lime-water. (Scheele.)

CYANIDE OF CERIUM.—Cyanide of potassium produces in solutions of cerous salts a white gummy precipitate, which however quickly gives off hydrocyanic acid and is converted into hydrated cerous oxide. (Beringer; *Ann. Pharm.* 42, 139.)

CYANIDE OF YTTRIUM.—The solution of hydrate of yttria in aqueous

hydrocyanic acid yields on evaporation white efflorescent nodules, easily soluble in water and alcohol. (Berlin.)

Hydrate of Alumina does not dissolve in aqueous hydrocyanic acid (Scheele); when cyanide of potassium is added to a salt of alumina, hydrate of alumina is precipitated free from hydrocyanic acid.

Cyanide of Titanium?—When the solution of crude platinum ore in aqua-regia is precipitated by cyanide of silver, cyanide of titanium is thrown down, together with the cyanide of palladium and copper. On igniting this precipitate in a retort, cyanide [or impure chloride ?] of titanium sublimes in the form of a greyish white mass, which dissolves readily in water, and is then precipitated white by ammonia, yellowish red by tincture of galls, and gives a white colour with tin and hydrochloric acid. (Fr. Weiss & Fr. Döbereiner, *Ann. Pharm.* 14, 16.)

¶ *Nitrocyanide of Titanium.*—$C^2NTi,3NTi^3$.—Formerly regarded as metallic titanium (III., 480).—Occurs as a furnace-product in the form of beautiful, opaque, copper-coloured crystals in the high blast-furnaces in which iron is smelted (III. 466, 467). Its production appears to be connected with the formation of cyanide of potassium so constantly observed in the iron furnaces (p. 380); a similar product is in fact obtained by placing a mixture of ferrocyanide of potassium and titanic acid in a well-closed crucible, and exposing it for an hour to a heat sufficient to melt nickel. The result is a brown unfused mass, which, under a magnifying power of 300 diameters, exhibits, besides particles of metallic iron, a network of short copper-coloured prisms having a strong metallic lustre. These crystals, when freed from iron by hydrochloric acid, exhibit all the properties of the crystals found in the blast furnaces. (Wöhler.) — [For the physical properties of this compound, *vid.* Vol. III., 468.]

					Wöhler.	Or:			
2 C	12	....	3·90	....	3·64	C^2NTi	50	....	16·23
4 N	56	....	18·18	....	18·30	$3NTi^3$	258	....	83·77
10 Ti	240	....	77·92	....	77·26				
Graphite		....		....	0·92				
	308	....	100·00	....	100·12		308	....	100·00

The graphite is merely an accidental admixture.—The crystals with which the analysis was made, were produced at the Rübeland smelting furnace in the Hartz, where a mass of this compound has been found weighing 80 lbs. (*comp.* III., 467.)

When this compound is heated to redness in a porcelain tube, and a continuous current of aqueous vapour passed over it, titanic acid is formed with evolution of hydrogen gas in considerable quantity (Regnault), and likewise of ammonia and hydrocyanic acid. (Wöhler.) If the crystals are in their natural state (not pulverized), the titanic acid thus produced maintains the form of rounded cubes; but these, when examined by the microscope, are found to consist of aggregates of crystals in the form of pointed, square-based octohedrons, having a strong lustre and exactly resembling the crystals of native anatase.

The crystals of nitrocyanide of titanium heated in dry chlorine gas, yield liquid chloride of titanium, and a crystalline, volatile, yellow sublimate, consisting of a compound of chloride of titanium with chloride of cyanogen.—Mixed in the state of powder with hydrate of potash and

fused, they give off ammonia, and are converted into titanate of potash. When the pulverized compound is heated with oxide of lead, copper, or mercury, a lively sparkling flame is emitted and the oxide is reduced to the metallic state. The heat evolved in this reaction is so great that even copper runs into a globule in the glass tube. (Wöhler, *Ann. Pharm.* 73, 347; *N. Ann. Chim. Phys.* 29, 166; abstr. *Berl. Acad. Ber.* 1849, 244; *Pogg.* 78, 401; *Pharm. Cent.* 1849, 822; *Chem. Soc. Qu. J.* 2, 352; *Chem. Gaz.* 1850, 73; *N. Ann. Chim. Phys.* 28, 382; *Compt. rend.* 29, 505; *Instit.* 1849, 353.) ¶

CYANIDE OF VANADIUM.—When hydrated vanadic oxide is digested in a close vessel with aqueous hydrocyanic acid, a dark brown gelatinous mass is produced, which may be washed and dried without turning green. It dissolves in aqueous cyanide of potassium; but the solution, when evaporated in an open vessel, continually gives off hydrocyanic acid and leaves vanadiate of potash. (Berzelius, *Pogg.* 22, 26.)

PROTOCYANIDE OF CHROMIUM, or CHROMOUS CYANIDE.—CrCy.—Formed by dissolving protochloride of chromium, CrCl, in water thoroughly freed from air by boiling and immediately pouring the solution into aqueous cyanide of potassium. The white precipitate does not dissolve in excess of cyanide of potassium. It oxidizes during washing, and is quickly converted into a greyish green compound of sesquioxide and sesquicyanide of chromium. (*Berzelius Lehrbuch.*)

SESQUICYANIDE OF CHROMIUM, or CHROMIC CYANIDE.—Cr^2Cy^3.—Formed by precipitating a chromic salt with cyanide of potassium. When neutral sesquichloride of chromium is added drop by drop to aqueous cyanide of potassium, a light bluish grey precipitate is formed, which is insoluble in excess of cyanide of potassium. If, on the contrary, the cyanide of potassium be dropped into the sesquichloride of chromium, the precipitate at first dissolves in excess of the latter; on further addition of cyanide of potassium, it becomes permanent in the cold, but dissolves when heated; a large quantity of cyanide of potassium, however, precipitates all the chromium. Similar reactions are obtained with potash chrome-alum, excepting that the mixture immediately becomes green.

The precipitate, which is white at first, soon unites into a bluish green mass, which becomes somewhat darker after being washed and dried. When a dilute solution of cyanide of potassium is dropped into alcoholic sesquichloride of chromium; the resulting precipitate is gelatinous and of a dark violet colour, but becomes black after drying; it has a conchoidal fracture, and forms a bluish grey powder.

Sesquicyanide of chromium, after being dried in an atmosphere of hydrogen, at a temperature about 200°, which causes it to shrink together strongly, may be afterwards kept in hydrogen gas, at a continued red heat, without decomposition. It then dissolves (with the exception of a slight product of decomposition) in boiling hydrochloric acid, forming a green solution, from which it is precipitated by ammonia, with its original bluish grey colour. Recently precipitated sesquicyanide of chromium likewise dissolves in dilute acids, even in acetic acid, forming green solutions, from which nothing is separated by ether. Hot potash-ley decomposes the compound into chromic oxide and sesquicyanide of chromium and potassium. (*Berzelius Lehrbuch.*)

Aqueous cyanide of potassium, mixed at ordinary temperatures with

sulphate of chromic oxide and potash, gives off hydrocyanic acid, and forms a greyish white precipitate, which afterwards becomes dark green, and when dissolved in nitric acid, throws down cyanide of silver from the nitrate. (F. & E. Rodgers.) After the precipitate, which has the appearance of hydrated chromic oxide, has been well washed, its solution in nitric acid no longer precipitates silver. (Rammelsberg, *Pogg.* 42, 141.)

Hydro-chromidcyanic acid. $3HCy,Cr^2Cy^3 = C^6N^3H^3,C^6N^3Cr^2$.—Formed by passing sulphuretted hydrogen gas through water, in which finely divided sesquicyanide of chromium and silver is suspended, filtering to separate the sulphide of silver, and evaporating in vacuo. Crystalline, reddens litmus strongly, and decomposes carbonates. (Böckmann.)

Chromidcyanide of Potassium. $3KCy,Cr^2Cy^3 = C^6N^3K^3,C^6N^3Cr^2$.—*Sesquicyanide of Chromium and Potassium.*—The solution of hydrated chromic oxide in aqueous potash which is supersaturated with hydrocyanic acid, acquires a brown-red colour on exposure to the air, and yields crystals, which may be purified by recrystallization. These crystals are yellow, and have the form of ferridcyanide of potassium. (Böckmann, *Liebig, Chim. org.* 1, 174.)

This salt is likewise formed on supersaturating a chromic salt with a large quantity of cyanide of potassium, till, on the application of heat, the precipitate redissolves, and forms a yellow solution. (Haidlen & Fresenius.) When washed and still moist sesquicyanide of chromium is digested, over the water-bath, with aqueous cyanide of potassium in a bottle filled with the liquid and closed, the liquid slowly acquires a deep yellow colour, without dissolving any of the cyanide of chromium. The compound is most readily obtained by digesting the red powder of sesquichloride of chromium and potassium, with aqueous cyanide of potassium at 80° or 90°, till the separated sesquicyanide of chromium is redissolved, adding alcohol in small portions to the filtrate, as long as a soft yellow mass continues to settle down (afterwards white flakes of cyanide of potassium are precipitated); collecting the yellow mass by itself; dissolving it in a very small quantity of water; and leaving the yellow solution to evaporate in the air. In this case, the chromidcyanide of potassium crystallizes indistinctly, mixed with bluish grey sesquicyanide of chromium, from which, however, it may be separated by solution in water. The yellow solution when left to evaporate spontaneously in the air, deposits violet sesquicyanide of chromium; but when mixed with a small quantity of sal-ammoniac, and then evaporated, it gives off hydrocyanate of ammonia, and deposits bluish grey sesquicyanide of chromium. (*Berzelius Lehrb.*)

Recently precipitated *Hydrate of Uranous Oxide* does not dissolve in aqueous hydrocyanic acid. On adding aqueous cyanide of potassium to protochloride of uranium, hydrocyanic acid is given off, and a black precipitate formed, consisting of uranous oxide free from hydrocyanic acid. (Rammelsberg, *Pogg.* 59, 2.)

Sesquicyanide of Uranium? Cyanide of potassium forms a yellowish white precipitate with uranic salts (Proust); the precipitate has a splendid yellow colour, and dissolves in nitric acid. (F. & E. Rodgers.) It likewise dissolves very sparingly in excess of cyanide of potassium, forming a pale yellow liquid, which acquires a deeper yellow colour when treated with hydrocyanic acid, but retains the odour of that acid. (F. & E.

Rodgers.) The solution of the precipitate in cyanide of potassium is accelerated by heat, the yellow liquid is not precipitated by acids. (Haidlen & Fresenius; *comp.* also Wittstein, *Repert.* 63, 214.)

PROTOCYANIDE OF MANGANESE, or MANGANOUS CYANIDE.—MnCy.—Cyanide of potassium forms with manganous salts, a greyish yellow (Ittner), yellow (Proust), yellowish white (Wittstein), greyish green (Rammelsberg), faintly reddish white (Gm.), bulky precipitate. It quickly turns brown on exposure to the air. (Rammelsberg, *Pogg.* 42, 117.) It is decomposed by the stronger acids, and dissolves in alkaline hydrocyanate. (Ittner.)

MANGANOSO-MANGANIC CYANIDE.—$Mn^5Cy^6 = C^6N^3Mn^3, C^6N^3Mn^2$.—The reddish yellow precipitate which manganico-potassic cyanide forms with manganous salts. (Rammelsberg.)

SESQUICYANIDE OF MANGANESE, or MANGANIC CYANIDE.—$Mn^2Cy^3 = C^6N^3Mn^2$. Known only in combination with other metallic cyanides.

Manganocyanide of Potassium. Protocyanide of Manganese and Potassium.—The brown-red solution of manganous cyanide in cyanide of potassium, deposits the former on the addition of a moderate quantity of acid; on exposure to the air it deposits hydrated manganous oxide, and is converted into the following compound. Recently precipitated sulphide of manganese dissolves slowly and sparingly in heated aqueous cyanide of potassium, forming a pale reddish yellow liquid, containing sulphide of potassium and manganocyanide of potassium. (Haidlen & Fresenius, *Ann. Pharm.* 43, 122.)

Manganidcyanide of Potassium. $3KCy, Mn^2Cy^3 = C^3N^3K^3, C^6N^3Mn^2$.—*Sesquicyanide of Manganese and Potassium.*—Obtained by leaving a solution of protocyanide of manganese in aqueous cyanide of potassium to evaporate in the air till it crystallizes.—1. Manganous carbonate is digested with aqueous cyanide of potassium and hydrocyanic acid in an open vessel, or the precipitate obtained by adding cyanide of potassium to manganous sulphate is dissolved in aqueous cyanide of potassium, and the reddish filtrate carefully evaporated. (Gm.)—2. A concentrated solution of manganous acetate is mixed with a large quantity of hydrocyanic acid, and neutralized with potash, and the colourless or pale yellow filtrate, containing protocyanide of manganese, is evaporated at a gentle heat, whereupon it is suddenly converted (even out of contact of air, and, therefore, perhaps with evolution of hydrogen) into a red-brown solution of manganic-potassic cyanide, a black precipitate of hydrated manganic oxide being formed at the same time; this solution is then filtered and evaporated to the crystallizing point. (Rammelsberg.) Recently precipitated protocyanide of manganese dissolves but sparingly in aqueous cyanide of potassium; but after it has acquired a darker colour by exposure to the air, it dissolves abundantly, and the solution, when evaporated, yields long needles. (Balard.)

Brown-red needles (Gm.) having the form of ferridcyanide of potassium. (Rammelsberg.) They turn brown in the air; their red aqueous solution becomes turbid when exposed to the air, and gradually deposits the manganese, in the shape of black hydrated sesquioxide, the change being accelerated by repeated solution and evaporation. (Gm. *Handbuch*, Aufl. 2, II., 1694.) The crystals decompose when heated above 200°, turning black, giving off a small quantity of hydrocyanic acid, and

leaving a brown-red alkaline residue. Acids liberate hydrocyanic acid from the salt; alkalis are without action upon it; hydrosulphate of ammonia very slowly precipitates a portion of the manganese. (Rammelsberg, *Pogg.* 42, 117.) The crystals are decomposed by water or alcohol, and must, therefore, be dissolved in aqueous cyanide of potassium. (Balard, *Compt. rend.* 19, 919.)

	Crystallized.			Rammelsberg.
3 K	117·6	....	35·68	35·44
2 Mn	56·0	....	16·99	16·54
6 Cy	156·0	....	47·33	
$C^6N^3K^2,C^6N^3Mn^2$	329·6	....	100·00	

Hydrocyanate of lime, added to *Hydrochlorate of Antimonic Oxide*, throws down the pure oxide with evolution of hydrocyanic acid (Scheele); cyanide of potassium acts in the same manner. Tersulphide of antimony dissolves slowly in boiling aqueous cyanide of potassium; the pentasulphide of antimony dissolves readily; and both are precipitated in the original state by acids. (Haidlen & Fresenius.)—From *Bismuth-salts* also alkaline hydrocyanates do not throw down cyanide, but only oxide of bismuth. (Haidlen & Fresenius.)—¶ Th. Diez (*Jahrb. pr. Pharm.* 22, 80; *Jahresber.* 1851, 379) states that cyanide of bismuth is obtained as a somewhat yellowish precipitate, on adding cyanide of potassium to pure nitrate of bismuth; the liquid, when left at rest, deposits a considerable additional quantity of the cyanide in small crystals; hence it should not be filtered till the following day. Diez, however, gives no experiment to demonstrate the existence of cyanogen in his precipitate. Hydrocyanic acid produces no precipitate in solution of acetate of bismuth. ¶—Sulphide of bismuth does not dissolve in aqueous cyanide of potassium.

Cyanide of Zinc.—ZnCy.—Even the oxide of zinc produced by combustion is converted into cyanide of zinc by digestion in aqueous hydrocyanic acid. Alkaline hydrocyanates added to zinc-salts, throw down white cyanide of zinc (Scheele), and the same compound is precipitated from acetate of zinc by free hydrocyanic acid. (Wöhler.)

Preparation. 1. By bringing oxide of zinc in contact with hydrocyanic acid.—2 parts of ferrocyanide of potassium are distilled with the requisite quantity of dilute sulphuric acid, and the hydrocyanic acid collected in a well-cooled receiver, containing 1 pt. of flowers of zinc, together with water, and frequently agitated; when the odour of hydrocyanic acid becomes permanent, the oxide may be considered as saturated. (Corriol & Berthemot, *J. Pharm.* 16, 444; also *Br. Arch.* 35, 152; also *Repert.* 36, 106.) An equally good method is to shake up oxide of zinc with aqueous hydrocyanic acid.—2. By precipitating acetate of zinc with aqueous hydrocyanic acid. In this case, only half of the zinc is thrown down in the form of cyanide, because the acetic acid which is set free prevents further precipitation. Hence it is necessary to neutralize the acetic acid repeatedly, by adding small quantities of carbonate of lime. (Corriol & Berthemot.) Instead of acetate of zinc, a mixture of sulphate of zinc with acetate of potash may be used. (Bette, *Ann. Pharm.* 31, 214.)—3. By precipitating a zinc-salt with an alkaline hydrocyanate. This salt must be free from ferrocyanide, also from carbonate or cyanate, otherwise ferrocyanide or carbonate of zinc will be precipitated together with the cyanide. Bette passes the vapour of

hydrocyanic acid evolved from 17 pts. of ferrocyanide of potassium, 17 oil of vitriol, and 32 water, into a receiver containing 24 pts. of aqueous ammonia of sp. gr. 0·97; adds the hydrocyanate of ammonia thereby produced to a solution of 18 pts. sulphate of zinc in 48 water; and washes the precipitated cyanide of zinc, which, when dry, amounts to 7 parts. O. Henry (*J. Pharm.* 15, 57) mixes aqueous sulphate of zinc with the aqueous solution of the cyanide of potassium obtained by igniting the ferrocyanide. Schindler (*Mag. Pharm.* 36, 67) precipitates chloride or nitrate of zinc with hydrocyanate of lime, prepared in the manner which he recommends (p. 417); and washes the precipitate only so long as the wash-water still contains zinc. If the washing be continued longer, the precipitate becomes more and more basic, because the water takes up hydrocyanic acid, and leaves the zinc-oxide in the precipitate; the loosely coherent precipitate is then dried, during which process hydrocyanic acid is likewise given off. Hence the cyanide of zinc contains a larger quantity of oxide, as the solution from which it has been precipitated is more dilute. Thus the precipitate obtained from concentrated solutions, contains 88·90 per cent. of cyanide of zinc, 9·06 of oxide, and 2·04 water; the precipitate from solutions of the two precipitants in 40 parts of water, contains 54·40 cyanide of zinc, 37·32 oxide, and 8·25 water. The precipitate is free from carbonic acid, provided it has been quickly dried, and the cyanide of potassium used was free from carbonate of potash. (Schindler.) According to Rammelsberg (*Pogg.* 42, 114), on the contrary, the cyanide of zinc is anhydrous, and contains 55·76 per cent. of zinc.

Snow-white, tasteless powder.

Cyanide of zinc, heated in close vessels, gives off cyanogen gas as long as water continues to escape from it, but not much afterwards. When perfectly dry, however, it still undergoes slight decomposition, and ultimately leaves a black mixture of cyanide of zinc (paracyanide, according to Rammelsberg), granules of metallic zinc, and charcoal. (Schindler.) Well dried cyanide of zinc, kept for four months, aggregates into a compact mass, smells strongly of ammonia, has a sweetish taste which after a while becomes metallic, and gives off 5 per cent. of ammonia; cyanide of zinc and ammonium appears, therefore, to have been formed. (Schindler.)—Cyanide of zinc dissolves in the stronger acids when cold and dilute (even in acetic acid, according to Haidl. & Fres.), with evolution of hydrocyanic acid. (Scheele.) It it but partially decomposed by continued boiling with mercuric oxide. (Corriol & Berthemot.) Insoluble in water and in alcohol; dissolves in aqueous ammonia or potash, forming mixtures of zincate of the alkali with cyanide of zinc and ammonium or potassium:

$$2ZnCy + 2KO = KO,ZnO + KCy,ZnCy.$$

It likewise dissolves in carbonate of ammonia, and, on the application of heat, in ammoniacal salts. (Wittstein, *Repert.* 63, 314.)—Dissolves readily in alkaline hydrocyanates.

Cyanide of Zinc and Ammonium.—$NH^4Cy,ZnCy$.—1. Obtained by leaving a solution of cyanide of zinc in aqueous ammonia [or in hydrocyanate of ammonia] to evaporate freely in the air.—2. By passing the vapour of hydrocyanic acid evolved from ferrocyanide of potassium and sulphuric acid into a receiver containing aqueous ammonia and oxide of zinc, and evaporating the filtrate.

Colourless rhombic prisms (differing but little from square prisms),

with truncated lateral edges. The crystals effloresce in the air, and smell strongly of hydrocyanic acid and ammonia. They give off hydrocyanate of ammonia, and, after ignition, leave a residue, which gives off ammonia when fused with hydrate of potash, and therefore still retains ammonia [cyanide of zinc]. Ignited in contact with air, they leave oxide of zinc. They dissolve imperfectly in water, with separation of cyanide of zinc; with acids they give off hydrocyanic acid. They dissolve completely in aqueous ammonia, and very sparingly in alcohol of 40° Bm. (Corriol & Berthemot, *J. Pharm.* 16, 444.)

Cyanide of Zinc and Potassium.—KCy,ZnCy.—Formed, when oxide or carbonate of zinc is dissolved in aqueous cyanide of potassium mixed with hydrocyanic acid. (Gm.) Recently precipitated sulphide of zinc dissolves in aqueous cyanide of potassium, forming this compound, together with sulphide of potassium. (Haidlen & Fresenius.)

Preparation. Cyanide of zinc is dissolved in aqueous cyanide of potassium, or oxide or carbonate of zinc in cyanide of potassium or carbonate of potash, mixed with hydrocyanic acid. The proportion must be such that the liquid shall smell but faintly of hydrocyanic acid, and have a scarcely perceptible alkaline reaction. The carbonic acid is expelled with brisk effervescence. Hydrocyanic acid may be added, with frequent agitation, to 40·2 pts. (1 At.) zinc-oxide and 69·2 pts. (9 At.) carbonate of potash, and water, till the acid retains its odour, and the oxide is dissolved. The crystals obtained from the solution by evaporation and cooling may be purified by recrystallization.

Large, regular octohedrons, sometimes transparent and colourless, sometimes turbid, decrepitating when heated, but fusing without decomposition into a transparent and colourless liquid. Permanent in the air. Slight alkaline reaction, when dissolved in water. (Gm. *Handbuch*, Aufl. 2, II., 1693.) Has a peculiar sweet taste. (Schindler, *Mag. Pharm.* 36, 70.) The aqueous solution smells slightly of hydrocyanic acid. Small quantities of hydrochloric, sulphuric, or acetic acid added to it, throw down cyanide of zinc, which is gradually decomposed and dissolved by larger quantities of the same acids. Sulphuretted hydrogen gas passed through the solution, precipitates but little sulphide of zinc. The warm aqueous solution smells faintly of hydrocyanic acid. (Gm.) With a concentrated solution of chloride of barium, this salt forms a precipitate which dissolves slowly in water; with a dilute solution, it gives no precipitate. The precipitate obtained with chloride of calcium dissolves in excess of that salt. Cobalt-salts yield a pale brick-red, nickel-salts a greenish white, and corrosive sublimate a white precipitate, no perceptible odour of hydrocyanic acid being evolved in either case. These precipitates are, therefore, compounds of cyanide of zinc with other cyanides. (Gm.) But in the precipitation of alum, of hydrochlorate of titanic, chromic or ferric oxide, or of mercurous nitrate, hydrocyanic acid is set free, and the precipitate consists entirely of the oxide or its hydrate. Sulphate of copper gives a brownish yellow precipitate, which evolves cyanogen, and is probably, therefore, a mixture of cyanide of copper and cyanide of zinc. (Gm.) The precipitate formed with acetate of lead is a white powder, from which acetic acid extracts oxide of lead, leaving cyanide of zinc undissolved; hence, perhaps, the precipitate is ZnCy,PbO. (Samselius, Berzelius, *Jahresber.* 20, 152.)—Alcohol added to the aqueous solution, throws down bitartrate of potash; probably, therefore, a zinco-hydrocyanic HCy,ZnCy is produced. (F. & E. Rodgers.) Cyanide of

zinc and potassium dissolves readily in cold water, and not much more abundantly in hot water. (Gm.)

	Dried Crystals.			Rammelsberg.		Schindler.
K	39·2	....	31·77	32·15	.....	31·3
Zn	32·2	....	26·09	25·91	.....	26·0
2 Cy	52·0	....	42·14	.....	.....	42·4
KCy,ZnCy	123·4	....	100·00	.....	.....	99·7

The author's analyses give similar results. The crystals contain no combined water, but only water of decrepitation, amounting, according to Schindler's experiments, to 2 or 3 per cent.; but according to the author's, to only ½ per cent. Rammelsberg (*Pogg.* 38, 371) dried the crystals at 200°.

This salt, from the invariability of its composition and the facility with which hydrocyanic acid is separated from it by acids, is better adapted for medicinal use than hydrocyanic acid itself.

Cyanide of Zinc and Sodium.—NaCy,2ZnCy.—Prepared in a similar manner to the potassium-compound. When much concentrated, it crystallizes in white, shining laminæ, which at 200° give off all their water of crystallization, amounting to 22·79 per cent. (5 At.). Dissolves in water much more readily than the potassium-salt. (Rammelsberg, *Pogg.* 42, 112.)

	Dehydrated.			Rammelsberg, at 200°.
Na	23·2	....	14·01	..... 14·79
2 Zn	64·4	....	38·89	..... 37·89
2 Cy	78·0	....	47·10	
NaCy,2ZnCy	165·6	....	100·00	

Cyanide of Zinc and Barium.—The potassium-compound added to acetate of baryta, throws down a white powder, which dissolves very slowly in water, does not appear to contain water, and appears to consist of: BaCy,2ZnCy; it contains, however, ½ per cent. potassium. (Rammelsberg, *Pogg.* 42, 113; *comp.* Samselius, *Berzelius Jahresbericht*, 20, 152.)

Cyanide of Zinc and Calcium.—Obtained by treating cyanide of zinc with hydrocyanate of lime; tolerably soluble. (Schindler, *Mag. Pharm.* 36, 70.)

Chromidcyanide of Zinc.—Chromidcyanide of potassium forms with zinc-salts, a white precipitate which turns light bluish grey when dry. (*Berzelius Lehrb.*)

Manganidcyanide of Zinc.—Manganidcyanide of potassium gives a rose-coloured precipitate with zinc-salts. (Balard.)

CYANIDE OF CADMIUM.—CdCy. In consequence of the solubility of cyanide of cadmium in water, cadmium-salts are not precipitated by alkaline hydrocyanates.—Cyanide of cadmium is prepared by dissolving recently precipitated and well washed hydrated oxide of cadmium in hydrocyanic acid, and evaporating the filtrate at a gentle heat till it crystallizes.—White crystals, which are permanent in the air, contain no water, undergo no alteration at 200°, but when more strongly heated in contact with air, turn brown and black, and become covered with a thick deposit of oxide. (Rammelsberg, *Pogg.* 38, 364.)

According to Wittstein, cyanide of potassium forms, with sulphate of cadmium, a white precipitate, soluble in warm ammonia, insoluble in ammoniacal salts; according to Haidlen & Fresenius, it forms a yellowish white precipitate of cyanide of cadmium. [The author likewise obtained with sulphate of cadmium and cyanide of potassium, a copious white precipitate, soluble in excess of cyanide of potassium. What difference is there between this precipitate and the soluble compound obtained by Rammelsberg?]

				Rammelsberg.
Cd	56	68·29		67·26
Cy	26	31·71		
CdCy	82	100·00		

Cyanide of Cadmium and Potassium.—KCy,CdCy.—Obtained by evaporating and cooling a mixture of acetate of cadmium and cyanide of potassium. Colourless octohedrons, having a strong lustre, and exactly like the zinc-salt; permanent in the air; taste metallic, and like hydrocyanic acid. At 200°, the crystals give off from 0·6 to 3·1 per cent. of mechanically enclosed water, and when more strongly heated, fuse into a colourless liquid, which on cooling solidifies into a grey crystalline mass. (Rammelsberg.)

			Rammelsberg, at 200°.
K	39·2	26·63	26·58
Cd	56·0	38·04	37·27
2 Cy	52·0	35·33	
KCy,CdCy	147·2	100·00	

When heated above its melting point in a close vessel, it decomposes very slowly; but if exposed to the air, it gives off brown fumes of oxide of cadmium, deposits metallic cadmium on the sides of the vessel, and leaves a carbonaceous, alkaline residue. Oil of vitriol acts violently upon it; dilute sulphuric, hydrochloric, or nitric acid liberates hydrocyanic acid from it, even at ordinary temperatures. Sulphuretted hydrogen passed through the aqueous solution, precipitates the cadmium completely in the form of yellow, finely divided sulphide, which passes with the liquid through the filter, unless the liquid be mixed with a stronger acid, or left to stand for some time. Hydrochlorate of baryta, strontia, or lime, forms with it a white precipitate, soluble in hydrochloric acid; sulphate of manganese throws down white flakes, which soon turn brown; tartar-emetic or nitrate of bismuth, a white precipitate; sulphate of zinc, a white precipitate soluble in acids, and containing, after washing, 4 pts. zinc to 1 pt. cadmium; and sulphate of copper, a brownish white precipitate, with evolution of cyanogen. From mercurous nitrate the solution throws down metallic mercury. Solution of gold is decolorized by it, with evolution of cyanogen, but without precipitation. From alum and ferric sulphate the solution throws down the hydrated oxides, with evolution of hydrocyanic acid. No reaction is exhibited by ammonia, potash, sulphate of magnesia, or corrosive sublimate. Cyanide of cadmium and potassium dissolves in 3 parts of cold water, 1 part of boiling water, and not perceptibly in absolute alcohol. (Rammelsberg, *Pogg.* 38, 366.)

Manganidcyanide of Cadmium.—Cadmic salts acquire a rose-colour when treated with *manganid*-cyanide of potassium. (Balard.)

When stannous or stannic salts are treated with hydrocyanate of lime

or potash, the precipitate does not contain cyanide of tin, but merely hydrated stannous or stannic oxide. (Scheele, Ittner.) A certain portion of tin, however, remains dissolved in the hydrocyanate of potash. Protosulphide of tin likewise dissolves to a slight extent in boiling aqueous cyanide of potassium, and is reprecipitated by hydrochloric acid; bisulphide of tin also dissolves, with separation of hydrated stannic oxide. (Haidlen & Fresenius.)

CYANIDE OF LEAD.—PbCy.—Hydrocyanate of lime forms with neutral acetate of lead a white precipitate, which is insoluble in water and in hydrocyanate of lime, but dissolves in nitric acid, with evolution of hydrocyanic acid. (Scheele.) Hydrocyanic likewise forms with sugar of lead a thick white precipitate, which dissolves very sparingly in cold water, more abundantly in hot water, leaving however a pale red residue. (F. & E. Rodgers.)—Nitrate of lead is also precipitated by hydrocyanic acid. The white precipitate forms turbid mixtures with aqueous ammonia, carbonate of ammonia, and nitrate of ammonia, but with hot aqueous hydrochlorate or succinate of ammonia, it forms a clear solution which becomes turbid as it cools. (Wittstein.)—¶ According to Erlenmeyer (*J. pr. Chem.* 48, 356) hydrocyanic acid produces no precipitate either in nitrate, neutral acetate, or basic acetate of lead. Hydrocyanate of ammonia forms a slight yellowish precipitate in solution of neutral acetate of lead. ¶—Cyanide of lead ignited out of contact of air, gives off nitrogen gas and leaves a compound [or mixture] of lead and charcoal, which, if the heat applied has not been too strong, is pyrophoric. (Berzelius.)—When suspended in water, it is resolved by chlorine into chloride of lead and free cyanogen, no chloride of cyanogen being formed so long as any cyanide of lead remains undecomposed. (Liebig, *Pogg.* 15, 571.) —It is decomposed by cold dilute sulphuric acid, with evolution of hydrocyanic acid.

¶ *Oxycyanide of Lead.* 2PbO,PbCy.—*Basic Cyanide of Lead.*—Obtained by adding ammonia to a mixture of basic acetate of lead and hydrocyanic acid. (Kugler, *Ann. Pharm.* 66, 265; *Jahresber.* 1847–8, 477; Erlenmeyer, *J. pr. Chem.* 48, 356; *Ann. Pharm.* 72, 265; *Jahresber.* 1849, 291.) White precipitate, which must be washed by decantation in a well-closed flask—during which operation it becomes yellowish white—and dried over sulphuric acid and lime. (Erlenmeyer.) Yellowish white (Kugler), smells of hydrocyanic acid (Erlenmeyer, Kugler), and gives off cyanogen when heated. (Kugler.)

			Erlenmeyer (mean).
2 C	12	3·39	3·35
N	14	3·95	3·90
3 Pb	312	88·14	88·09
2 O	16	4·52	4·56
2PbO,PbCy	354	100·00	

Or:			Erlenmeyer.	Or:			Erlenmeyer.
3 Pb	312	88·14	88·09	2 PbO	224	36·72	36·25
Cy	26	7·34	7·25	PbCy	130	63·28	63·64
2 O	16	4·52	4·56				
	354	100·00			354	100·00	

Kugler's analysis gives different results, viz., carbon 2·785; hydrogen 0·225;

nitrogen 2·34; lead 87·22; or 87·22 lead; 5·07 cyanogen; and 1·66 water; whence he deduces the formula PbO,PbCy + HO. This however requires 4·78 carbon; 5·58 nitrogen, and only 82·87 lead, or 10·36 cyanogen and 82·87 lead. The formula 3PbO,PbCy + HO, which requires 87·5 lead, 5·4 cyanogen, and 1·22 water, is more in accordance with Kugler's analysis; but as Kugler neglected the precaution of washing his precipitate out of contact of air, it may be concluded that his analysis was made with an impure substance. ¶

Chromidcyanide of Lead?—Chromidcyanide of potassium does not precipitate nitrate of lead, but with basic acetate of lead it forms a white precipitate (Böckmann); with lead-salts, it yields a white precipitate which becomes blue after drying. (*Berzelius Lehrbuch.*)

Manganidcyanide of Lead.—Manganidcyanide of potassium yields a brown precipitate with lead-salts. (Rammelsberg.)

Cyanide of Zinc and Lead.—Cyanide of zinc and potassium throws down from lead-salts a white powder, which is free from potassium, and appears to contain 2 At. cyanide of zinc to 1 At. cyanide of lead. (Rammelsberg, *Pogg.* 42, 114.)

Cyanide of Cadmium and Lead.—Sugar of lead forms with cyanide of cadmium and potassium a white precipitate which, before washing, contains 18·38 p. c. (1 At.) cadmium and 69·43 (2 At.)lead; but after being washed and then dried at 200°, whereby it loses only 0·55 p. c. water, it contains only 8·67 p. c. cadmium to 69·43 p. c. lead, therefore 1 At. to 4 At. (Rammelsberg.)

Compounds of Cyanide of Iron or Prusside of Iron.

SCHEELE. *Opuscula*, 2, 148.
ITTNER. *Beiträge zur Geschichte der Blausäure.* Freib. Const. 1809.
PROUST. *Ann. Chim.* 60, 185 and 225; also *N. Gehl.* 3, 549.
VAUQUELIN. *Ann. Chim. Phys.* 5, 113; also *Schw.* 25, 50.
BERZELIUS.—Ferrocyanides, Hydroferrocyanic acid, Prussian blue. *Ann. Chim. Phys.* 15, 144 and 225; also *Schw.* 30, 1.—Prussian blue, Ferrocyanide of lead. *Pogg.* 25, 385.
PORETT.—Hydroferrocyanates. *Phil. Trans.* 1814, 527; also *Schw.*, 17, 258; also *Gilb.* 53, 184; also *N. Tr.* 3, 2, 422.—*Ann. Phil.* 12, 214; also *Schw.* 26, 224.—*Ann. Phil.* 14, 295.
ROBIQUET.—Ferrocyanides. *Ann. Chim. Phys.* 12, 275; abst. *Schw.* 28, 110.—*Ann. Chim. Phys.* 17, 196.—Prussian blue. *Ann. Chim. Phys.* 44, 279; also *J. Pharm.* 16, 211; also *N. Tr.* 23, 2, 239.
THOMSON.—Ferrocyanide of Potassium. *Ann. Phil.* 12, 102; also *Schw.* 26, 203; also *N. Tr.* 3, 2, 469.—*Ann. Phil.* 15, 392; also *Schw.* 29, 504.—*Ann. Phil.* 16, 217.
GAY-LUSSAC.—Prussian blue. *Ann. Chim. Phys.* 46, 73.
L. GMELIN.—Ferridcyanide of Potassium. *Schw.* 34, 325.
PELOUZE.—Prussian green. *Ann. Chim. Phys.* 69, 40; also *J. Pharm.* 24, 545; abstr. *J. pr. Chem.* 16, 104.
RAMMELSBERG.—Ferrocyanides. *Pogg.* 38, 364; 42, 111.

BUNSEN.—Ferrocyanides with Ammonia. *Pogg.* 34, 131.—Ferrocyanides. *Pogg.* 36, 404.

WILLIAMSON.—Prussian blue, &c. *Ann. Pharm.* 57, 225.

FERROPRUSSIC OR HYDROFERROCYANIC ACID.—$C^6N^3FeH^3 = 2HCy, FeCy$.—*Ferruretted chyazic acid* (Porrett); *Eisenblausäure* (Gm.); *Dreifachblausaures Eisenoxydul*, *Wasserstoffeisencyanür* (Berzelius); *Ferrocyanwasserstoffsäure* (Liebig); *Acide hydrocyanoferrique* (Gay-Lussac).—Gay-Lussac and Liebig suppose that it contains a radical C^6N^3Fe, which the former calls *Cyanoferre*, the latter *Ferrocyanogen*, denoting it by the symbol Cfy.—This acid was discovered by Porrett in 1814.—*Formation?* According to Vauquelin, aqueous hydrocyanic acid, but not the anhydrous acid, brought in contact with iron in a close vessel, dissolves that metal, with evolution of hydrogen, and forms a liquid which, when exposed to the air, deposits prussian blue. The author's attempt to form such a liquid was not successful.

Preparation. 1. Porrett (*Schw.* 17, 262) dissolves ferrocyanide of barium in 1800 pts. of cold water, and precipitates the baryta by an exactly equivalent quantity of sulphuric acid, in a vessel protected from the air; the ferroprussic acid then remains in solution.—2. Porrett (*Schw.* 26, 224) mixes the solution of 50 grains of ferrocyanide of potassium in 2 or 3 drachms of hot water with the alcoholic solution of 58 grains of crystallized tartaric acid. The latter is completely precipitated in combination with the whole of the potash, in the form of cream of tartar, and the alcoholic liquid, when abandoned to spontaneous evaporation, deposits crystallized ferroprussic acid.—According to Berzelius, the methods 1 and 2 yield an impure product.—3. Robiquet (*Ann. Chim. Phys.* 12, 285) places prussian blue in contact with cold hydrochloric acid of the highest degree of concentration. This acid dissolves out all the sesquioxide of iron, and leaves ferroprussic acid, which must be washed by decantation with hydrochloric acid in a narrow cylindrical vessel, till the acid no longer acquires a perceptible colour by taking up oxide of iron. The product is then dried in a closed vessel filled with lime; dissolved in strong alcohol; the solution left to evaporate spontaneously; and the resulting crystals washed with a small quantity of alcohol, then dissolved in a large quantity, and the acid left to recrystallize.—4. Berzelius (*Schw.* 30, 44) passes sulphuretted hydrogen through water in which ferrocyanide of lead or ferrocyanide of copper recently precipitated and washed is suspended, continuing the passage of the gas till the solution contains an excess of it; then adds a sufficient quantity of ferrocyanide of lead to remove nearly all the excess of sulphuretted hydrogen, which would spoil the air-pump; filters quickly; and evaporates the colourless liquid in vacuo.—As the ferrocyanides of lead and copper always retain more or less ferrocyanide of potassium, even after long washing, they do not yield pure ferroprussic acid. (Gay-Lussac.)—5. Ferroprussic acid may be precipitated from its aqueous solution by the addition of a small quantity of ether; and thus the evaporation of the solution, during which it is difficult to exclude the air, may be dispensed with.—*a.* Ferrocyanide of lead is decomposed by sulphuretted hydrogen or sulphuric acid in presence of water; the filtrate agitated with a small quantity of ether, and set aside till the ferroprussic acid separates in the solid state; the liquid removed by means of a pipette; the acid washed on a filter with a mixture of ether and alcohol; afterwards pressed between paper; and the resulting white powder

dried in vacuo over oil of vitriol.—6. A concentrated aqueous solution of ferrocyanide of potassium is completely freed from air by boiling; then left to cool in a closed vessel; agitated with hydrochloric acid also freed from air by boiling, and afterwards with ether; the process continued as in *a*, excepting that the solid acid collected on the filter is dissolved in a small quantity of alcohol (to which a very small quantity of sulphuric acid may be added, to remove any potash that may be present); the syrupy solution filtered if not quite clear; and the ferroprussic acid separated from it by ether; then washed, as in *a*, with ether and alcohol, and afterwards pressed and dried in vacuo. (L. Posselt, *Ann. Pharm.* 42; 163.)—This method is also preferred by Berzelius.

Properties. When prepared by (4), it is milk-white, opaque, and amorphous. Reddens litmus, tastes agreeably sour, and afterwards somewhat rough; inodorous, provided no decomposition takes place. (Berzelius.)—Crystallizes, when the aqueous or alcoholic solution is left to evaporate freely, and according to Porrett (2), in cubes; according to Robiquet (3), in white, very sour, inodorous, probably tetrahedral crystals; according to Berzelius, when obtained by spontaneous evaporation of the saturated aqueous solution (4), it crystallizes in hydrated, apparently four-sided prisms, united in tufts.—The acid obtained by (5), is a yellowish or sometimes bluish white powder; but if a layer of ether be placed on the surface of its aqueous, or better of its alcoholic, solution, the acid separates at the surface of contact, in soft, snow-white, pearly laminæ. The concentrated aqueous solution, evaporated in vacuo, yields yellowish, tolerably hard, crystalline nodules. (Posselt.)

		Posselt.				
		a.	*b.*	Or:		
6 C	36	33·33	33·50	33·23	2 HCy	54 50
3 N	42	38·89				
Fe	28	25·93	25·08	25·22	FeCy	54 50
2 H	2	1·85	1·84	1·99		
$C^6N^3FeH^2$	108	100·00			2HCy,FeCy	108 100

The ferroprussic acid *a*, analyzed by Posselt, was dried in vacuo at the medium temperature; *b*, at 100°, at which temperature it suffered no decrease in weight. These analyses confirm the views of Gay-Lussac and Robiquet respecting the constitution of the acid. Berzelius formerly supposed it to contain 1HO more, according to which supposition it would be regarded as FeO,3HCy or 2HCy,FeCy+Aq. Gay-Lussac was the first who regarded it as a hydrogen-acid ($FeCy^3,H^2$) of the unknown radical $FeCy^3$=*Cyanoferre*.

Decompositions. Ferroprussic acid, when kept from the air, remains unaltered for a long time at 100°, till it gradually evolves anhydrous prussic acid, and leaves protocyanide of iron. This decomposition takes place more quickly in a stream of carbonic acid gas, or at a temperature much above 100°; when the heat is raised somewhat higher, the cyanide of iron likewise suffers decomposition. (Posselt.) Robiquet obtained anhydrous prussic acid, and a yellowish-brown, non-magnetic residue, which did not blacken when exposed to the air; gave off hydrocyanic acid when heated, together with a mixture of 1 vol. hydrogen and 2 vol. nitrogen, and left a residue of iron and charcoal, which did not give up any iron to sulphuric acid, but when treated with potash, gave off ammonia, and formed a very small quantity of ferrocyanide of potassium.

Berzelius's ferroprussic acid, dried in vacuo, and then heated, first gave off anhydrous prussic acid, and then carbonate and hydrocyanate of ammonia, and left bicarbide of iron. ¶ Rammelsberg (*Pogg.* 83, 80) obtained water and hydrocyanic acid, together with a residue of protocyanide of iron, which at a higher temperature was resolved into paracyanogen and a compound containing $C^{20}N^5Fe^{12}$. ¶—2. The aqueous solution of ferroprussic acid gives off hydrocyanic acid when boiled, and deposits white protocyanide of iron; but long boiling is required to complete the decomposition. (Berzelius.) According to Porrett, the same decomposition likewise takes place under the influence of light.—3. The dry acid remains unaltered in close vessels; but when exposed to the air, it gives off hydrocyanic acid, first becoming greenish, and afterwards being converted into prussian blue; in a similar manner, the aqueous solution deposits prussian blue when exposed to the air. (Berzelius.) Probably thus:

$$14C^6N^3FeH^2 + 4O = 2(C^6N^3Fe^3,2C^6N^3Fe^3) + 24C^2NH + 4HO.$$

The acid, when perfectly dry, remains unaltered in the air for a considerable time. (Posselt.)—4. With most salifiable bases, aqueous hydroferrocyanic acid immediately forms ferroprussiates, hydroferrocyanates, or ferrocyanides:

$$C^6N^3FeH^2 + 2MO = C^6N^3FeM^2 + 2HO.$$

From carbonates and acetates it expels the acid, even without the aid of heat. (Porrett.)—It even decomposes tartrates and oxalates. (Posselt.) It likewise throws down protocyanide of iron from the protochloride, and prussian blue from the sesquichloride (Döbereiner):

$$C^6N^3FeH^2 + 2FeCl = C^6N^3Fe^3 + 2HCl;$$

and,

$$3C^6N^3FeH^2 + 2Fe^2Cl^3 = C^6N^3Fe^3,2C^6N^3Fe^3 + 6HCl.$$

On mercuric oxide, ferroprussic acts only when heated, the two bodies being then resolved into cyanide of mercury and protocyanide of iron, which latter is then further oxidized by the excess of mercuric oxide, the mercury being at the same time reduced to the metallic state (Posselt):

$$3C^6N^3FeH^2 + 6HgO = 6C^2NHg + C^6N^3Fe^3 + 6HO.$$

Hence it appears that the cyanogen in the form of prussian, C^6N^3, is not capable of combining with mercury, such combination being possible only when the cyanogen is in the simple state of C^2N.

Combinations. *a.* Ferroprussic acid dissolves readily in water, forming a colourless solution if the water has been thoroughly freed from air by boiling. (Berzelius.) The concentrated solution is a transparent and colourless syrup, and likewise forms prussian blue when exposed to the air. A small quantity of ether causes the solution, if not too dilute, to coagulate in a thickish mass, from which the hydroferrocyanic acid separates.—*b.* The acid dried in vacuo dissolves in oil of vitriol, forming a colourless liquid which does not smell of hydrocyanic acid; this liquid, when exposed to the air, absorbs water, and solidifies into a white crystalline compound of sulphuric and ferroprussic acid, which is perfectly soluble in water: and in this solution the ferroprussic acid suffers, on exposure to the air, the same decomposition that it would undergo if dissolved in water alone. (Berzelius.) Alcohol also dissolves ferroprussic acid

readily and without colour (Robiquet), and ether throws it down from the alcoholic solution (Posselt.)

PROTOCYANIDE OF IRON, or FERROUS CYANIDE.—$C^6N^3Fe^3$ or FeCy.—*Eisencyanür* (Berzelius); *Ferrocyaneisen* (Liebig).

When aqueous cyanide of potassium is mixed with a ferrous salt free from ferric oxide, a light red-brown precipitate is obtained, which dissolves in acids. The composition of this precipitate requires further investigation: but it is, perhaps, the true protocyanide of iron, C^2NFe, whereas the lighter-coloured substance here to be considered, which is insoluble in acids, is prussiate of iron, $C^6N^3Fe^3$. From an aqueous solution of acid ferrous carbonate, hydrocyanic acid throws down a greenish cyanide of iron, which turns blue on exposure to the air. (Scheele, *Opusc.* 2, 164.)

1. When ferrocyanide of ammonium is carefully heated in close vessels till all the hydrocyanate of ammonia is volatilized, this compound remains in the form of a greyish-yellow substance (or greenish-yellow, if the air has not been completely excluded). May be kept undecomposed. When more strongly heated in contact with air, it turns brown, and is then converted into black bicarbide of iron, which, at a still higher temperature, exhibits a glimmering light, and if heated in the air, burns like tinder, and is converted into an equal weight of ferric oxide, because $1\frac{1}{2}$. 8 pts. of oxygen take the place of 2.6 pts. of carbon. (Berzelius, *Schw.* 30, 28.)

2. Pure prussian blue in a fine state of division, enclosed in a bottle with sulphuretted hydrogen-water, is converted into yellow, shining, crystalline granules of protocyanide of iron, which again turn blue on exposure to the air. (Robiquet.) Berzelius obtained by this process merely a white mass, which yielded ferroprussic acid on being treated with water.

3. On boiling a solution of ferroprussic acid, white protocyanide of iron is deposited (Berzelius.)

4. Ferroprussic acid heated in an atmosphere of carbonic acid to 100° or very little higher, leaves a residue of protocyanide of iron, which however is likewise decomposed at a few degrees above 100° (L. Posselt, *Ann. Pharm.* 42, 166.)

5. Aqueous ferroprussic acid, heated with mercuric oxide, forms cyanide of mercury and white protocyanide of iron (Posselt.)

Protocyanide of iron dissolves in aqueous alkalis, forming a compound of 1 At. cyanide of iron with 2 At. cyanide of the alkali-metal, while 2 At. protoxide of iron remain:

$$C^6N^3Fe^3 + 2KO = C^6N^3Fe^3K^2 + 2FeO,$$

or,

$$3FeCy + 2KO = 2KCy,FeCy + 2FeO.$$

Boiled with strong hydrochloric acid, it gives off hydrocyanic acid; but by dilute hydrochloric or sulphuric acid, it is neither dissolved nor decomposed.

FERROCYANIDES.—$C^6N^3FeM^2$.—*Ferroprussiates, Hydroferrocyanates, Eisenblausaure Salze, Ferrocyanüre, Cyanoferrures* (Gay-Lussac); in the hydrated state: *Ter-hydrocyanates, Double salts of ferrous hydrocyanate, Drehfach blausaure Salze, blausaure Eisenoxyduldoppelsalze, Hydrocyanoferrates* (Gay-Lussac).

These compounds may be regarded: 1. As *Prussian*, $C^6N^3H^3$, in which 1H is replaced by Fe and 2H by 2 At. of another metal.—2. As

compounds of 1 At. protocyanide of iron with 2 At. of another cyanide: 2MCy,FeCy.—3. As compounds of 1 At. ferroprussic acid with 2 At. of a metallic oxide *minus* 2 At. water. The ferroprussic acid is here regarded as a bibasic hydrogen-acid, in which 2 At. hydrogen may be replaced by 2 At. of a metal.—4. In the hydrated state, also, as compounds of 1 At. hydrocyanate of ferrous oxide with 2 At. hydrocyanate of another metallic oxide: *e. g.*, 2(KO,HCy)+FeO,HCy.

The ferrocyanides of the alkali-metals are obtained by neutralizing ferroprussic acid with caustic alkalis or alkaline carbonates; by dissolving protocyanide of iron in aqueous solutions of alkaline hydrocyanates, or in a mixture of alkaline carbonate and hydrocyanic acid; by treating protocyanide of iron, or a mixture of that compound with the sesquicyanide (prussian blue), with an aqueous alkali, whereby protoxide or sesquioxide of iron is formed; or by treating protoxide of iron with the aqueous solution of the cyanide of an alkali-metal, in which it dissolves with formation of alkali. The insoluble ferrocyanides are obtained by precipitating a soluble cyanide with the solution of the salt of an earth-metal or a heavy metal: *e.g.*, the copper-compound (*Scheme* 56 and 57):

$$2KCy,FeCy + 2(CuO,SO^3) = 2CuCy,FeCy + 2(KO,SO^3).$$

The ferrocyanides of the alkali-metals are colourless in the anhydrous, but yellow in the hydrated state; they exert no action on vegetable colours, have a faintly saline and bitter taste, and do not exhibit the violent action of hydrocyanic acid on the animal economy. The ferrocyanides of the earth-metals are white; and among those of the heavy metals some are white, while others are distinguished by bright colours. Hence the use of alkaline ferrocyanides to discover the presence of titanium, tantalum, molybdenum, uranium, iron, cobalt, nickel, and copper; but antimony, tellurium, platinum, rhodium, and iridium are not precipitated by alkaline ferrocyanides.

Those ferrocyanides which are deprived of all their water by a gentle heat, are decomposed at a higher temperature in the following manner: The cyanide of iron is always converted into carbide of iron, with evolution of nitrogen gas; but the other cyanide which is associated with it, either remains undecomposed,—which is the case with cyanide of potassium,—or is resolved into nitrogen and a metallic carbide, as with cyanide of lead; or into cyanogen gas and metal, as with cyanide of silver. If, however, the ferrocyanides are not completely dehydrated before being subjected to destructive distillation, they give off hydrocyanic acid, carbonic acid, and ammonia, and leave the two metals, combined or mixed with a greater or smaller quantity of carbon. In the circuit of the voltaic battery, the aqueous solutions of the alkaline ferrocyanides yield alkali at the negative pole, and hydrocyanic acid and prussian blue at the positive pole, unless the positive polar wire is of copper, in which case the deposit there formed consists of cyanide of copper. (Porrett.) When ferrocyanides are heated with oil of vitriol to a temperature much above 100°, they give off, with strong effervescence, sulphurous acid, carbonic acid, and nitrogen gases, and leave a compound of sulphuric acid with ammonia, protoxide of iron [sesquioxide?], and the oxide of the other metal. (Berzelius.) Besides the gases just mentioned, a large quantity of carbonic oxide is evolved, and a small quantity of sulphate of ammonia volatilizes. (Bunsen, *Pogg.* 34, 132.) Thomson (*Schw.* 26, 306) obtained the carbonic oxide evolved in these decompositions, but from the experiments which he

made with it, he regarded it as a hydrogenated oxide of carbon.—The stronger acids withdraw the other metal from ferrocyanides, and thereby separate ferroprussic acid:

$$2KCy,FeCy + 2SO^3 + 2HO = 2HCy,FeCy + 2(KO,SO^3).$$

A similar effect is produced by sulphuretted hydrogen, if the other metal be precipitable from its solutions by that reagent:

$$2PbCy,FeCy + 2HS = 2HCy,FeCy + 2PbS.$$

Neither alkalis nor sulphuretted hydrogen decompose the cyanide of iron contained in ferrocyanides.

Most ferrocyanides unite in their entire state with oil of vitriol, forming a kind of salt, in which they constitute the base. Their powder soaked in cold oil of vitriol swells up to a pasty compound, with loss of colour, and considerable evolution of heat, and, according to the nature of the metal present, either dissolves completely in a large excess of the acid, or remains almost undissolved, forming a solid compound with it. These compounds remain undecomposed even at temperatures much above 100°. If a small quantity of water be added to the resulting solutions, *e.g.*, by exposing them to the air, they frequently deposit a crystalline compound, which contains less sulphuric acid, and when treated with a larger quantity of water, is resolved either into ferroprussic acid and a compound of sulphuric acid with the other metallic oxide, or into metallic ferrocyanide and dilute sulphuric acid. (Berzelius, *Schw.* 30, 35.)

Intermediate Compounds of Cyanide or Prusside of Iron, which may be regarded as compounds of Ferrous and Ferric Cyanide and Water, in various proportions.

$$xC^6N^3Fe^3, yC^6N^3Fe^2 + zHO.$$

These compounds, considered in the anhydrous state, are analogous to the several varieties of ferroso-ferric oxide. They cannot, however, be obtained free from water, which indeed they give up but partially even at the temperature at which they begin to decompose. Either all the water is intimately combined with them as water, or part of it by its constituents only; so that these bodies may be regarded as compounds of hydrocyanate of ferrous oxide with terhydrocyanate of ferric oxide, and often also with water in its entire state.

If ferrous cyanide be regarded as $C^6N^3Fe^3$, and ferric cyanide as $C^6N^3Fe^3$, the assumption of the nucleus-theory involves the difficulty, that, in the latter compound, 1 At. of the nucleus is wanting, and nevertheless the compound is not removed into another series. To obviate this difficulty, Laurent and Gerhardt suppose that iron has two different atomic weights; that in the compounds corresponding to the protoxide it enters as *Ferrosum*=Fe, with an atomic weight=28, and in the compounds corresponding to the sesquioxide, as *Ferricum*=*f*, with an atomic weight=$\frac{2}{3}$. 28=18$\frac{2}{3}$. (*Comp.* p. 409.) According to this supposition, the compound $C^6N^3Fe^2$ contains, not 2 At. *Ferrosum*, as expressed by the preceding formula, but 3 At. *Ferricum*, according to the formula $C^6N^3f^3$. It is hereby presupposed that the true atoms of iron weigh much less than 28 (H=1), and that they unite, sometimes in such number as to form the group or molecule, *Ferricum*, sometimes in a number 1$\frac{1}{2}$ times as great, to form the larger molecule, *Ferrosum*. Until, however, this doctrine, which strikes

so deeply into the very foundations of the atomic theory, shall be supported by other considerations (*comp.* pp. 173, 174), it may suffice to admit, as we have already done in the case of cyanogen, that in certain peculiar cases, a nucleus may continue to exist, even when one of the atoms necessary to its conformation is deficient, without being transformed into a compound belonging to another series.

It was long ago noticed by Scheele (*Opusc.* 2, 174) as somewhat remarkable that hydrocyanic acid does not precipitate green vitriol, and that nevertheless prussian blue [as well as protocyanide of iron] is not decomposed by dilute sulphuric acid. This circumstance is favourable to the supposition that in the formation of prussian blue, or of protocyanide of iron, cyanogen C^2N is converted into prussian C^6N^3, and in this form enters into more intimate combination with the iron. Hydrocyanic acid does not throw down prussian blue even from ferroso-ferric acetate [Duflos, *Kastn. Arch.* 14, 94, maintains the contrary], but gradually precipitates it, after producing a green turbidity, from a mixture of ferroso-ferric sulphate and acetate of soda, even if this liquid be slightly acidulated with acetic acid. It has already been mentioned that, according to Scheele, a mixture of hydrocyanic acid and ferrous carbonate yields, when exposed to the air, first a green and then a blue precipitate.

To these hydrated compounds of ferrous and ferric cyanide belong, Prussian blue A, Prussian blue B, and Prussian green.

Prussian Blue A.—$C^6N^3Fe^3,C^6N^3Fe^3 + HO = 3FeCy,Fe^2Cy^3 + xHO$.

Hydrated ⅓-cyanide of Iron.—Although this blue is called in England by the name of *Turnbull's Blue*, I cannot agree with Williamson (*Ann. Pharm.* 57, 234) in regarding Turnbull as its discoverer (comp. *Schw.* 34, 343).

Formation. 1. By precipitating a ferrous salt with ferricyanide of potassium:

$$C^6N^3K^3,C^6N^3Fe^2 + 3FeCl = C^6N^3Fe^3,C^6N^3F^2 + 3KCl;$$

or,

$$3KCy,Fe^2Cy^3 + 3FeCl + 3FeCy,Fe^2Cy^3 + 3KCl.$$

The precipitate carries down with it a portion of the ferricyanide, and consequently the wash-water acquires a bluish green colour, by dissolving ferricyanide of potassium, and through its medium a portion of the blue precipitate. (Gay-Lussac.) Even when the aqueous solution of the ferricyanide of potassium is added drop by drop to excess of ferrous chloride, and the precipitate washed with hot water, it still retains 5 per cent. of potassium. (*Vid. infra*, Analysis 1, *a*. Wöhler & Völckel.) When solution of green vitriol is added to excess of ferricyanide of potassium, and the precipitate carefully washed out of contact of air with boiling water, by which it is not decomposed, it still retains more than 5 per cent. of potassium. (*Vid. infra*, Analysis 1, *β*.) But if protochloride of iron in excess be precipitated by ferricyanide of potassium, and the precipitate digested for some time with the aqueous protochloride, the whole of the potassium may be extracted from it by boiling water. (*Vid. infra*, Analysis 1, *γ*. Williamson.) If the precipitate obtained with ferricyanide of potassium and excess of green vitriol free from ferric oxide, be washed, and then shaken up, while still moist, with water and a few drops of ferric chloride, it will not take up any iron from that compound. (Gm.)—2. The blue precipitate which ferriprussic acid produces with ferrous salts has probably the same composition.—3. When an aqueous solution of ferricyanide of potassium is mixed with oil of vitriol, and the

resulting green precipitate, consisting of ferric cyanide [prussian green?] and a small quantity of cyanide of potassium, is boiled for some time with excess of sulphuric acid—which converts a portion of the cyanogen into ammonia—and then thoroughly washed, a similar blue compound remains. (Williamson.) This blue is regarded by Williamson as a peculiar compound; but, according to his own analysis (3), it appears to be identical with prussian blue A.—4. Whether the blue precipitate which the brown aqueous mixture of a ferric salt with ferricyanide of potassium yields on the addition of sulphuretted hydrogen, sulphurous acid, and other substances capable of giving up hydrogen to part of the cyanogen, be prussian blue A or B, is a question not yet decided. In the former case the equation will be:

$$3Fe^2Cy^3 + 2H = Fe^5Cy^6 + H^2FeCy^3;$$

in the latter:

$$4Fe^2Cy^3 + 2H = Fe^7Cy^9 + H^2FeCy^3.$$

That the acid produced in this decomposition is not hydrocyanic, but hydroferrocyanic acid, may be concluded from the fact that, at ordinary temperatures, the blue mixture does not give off hydrocyanic acid till after several hours, but evolves it immediately, if heated over the water-bath.—5. A ferric salt mixed with ferrous salt forms, with ferrocyanide of potassium, a violet-blue precipitate of much finer colour than that produced by a pure ferric salt. In the former case perhaps the precipitate consists of prussian blue A:

$$2K^2FeCy^3 + Fe^3Cl^4 = Fe^5Cy^6 + 4KCl.$$

According to this equation, 1FeCl should be mixed with $1Fe^2Cl^3$ to produce this finer blue A.—Liebig states (*Pogg.* 24, 364) that in commerce there occurs a peculiarly beautiful copper-coloured prussian blue, which is prepared by dissolving 11 pts. (4 At.) of green vitriol in water; mixing it with hydrochloric acid and a quantity of chloride of lime sufficient to convert the whole of it into ferric salt; then adding 11 parts (4 At.) of unaltered green vitriol; precipitating the mixture with 20 pts. (nearly 5 At.) of ferrocyanide of potassium; washing the precipitate 6 times with water; stirring it up while yet moist with gum-water; and lastly, pressing it and drying by heat. The proportion of ferrous salt used in this process is somewhat greater than that which the preceding calculation shows to be required for the formation of prussian blue A:

$$4(FeO,SO^3) + 2(Fe^2O^3,3SO^3) + 5K^2FeCy^3 = 10(KO,SO^3) + Fe^{12}Cy^{15}.$$

If however we remember that an oxidizing action is exerted by the chloride of lime which may be in excess, and by the air, it will appear probable that this commercial blue approaches pretty nearly to pure prussian blue A.

This compound, when dry, is of a deep blue colour, with a tinge of copper-red. (Wöhler and Völckel, *Ann. Pharm.* 35, 359.)

	Pure, air dried.			Williamson.	
				(1, γ)	(3)
12 C	72	17·82		17·45	17·5
6 N	84	20·79			
5 Fe	140	34·65		34·50	33·4
K				trace	trace
12 HO	108	26·74		28·05	27·1
Fe^5Cy^6,12HO	404	100·00			

Containing potassium, supposed anhydrous.			Wöhler & Völckel. (1, *a*.)	*Air-dried.*	Wöhler & Völckel.	Williamson. (1, *β*.)
60 C	360	23·78	24·08	C		
30 N	420	27·75	28·10	N }	33·69	
22 Fe	616	40·70	39·64	Fe	25·59	33·60
3 K	117·6	7·77	8·18	K	5·28	5·1
				HO	35·44	
	1513·6	100·00	100·00		100·00	

Prussian blue A yields, when decomposed, 2½ times as much ferric oxide as the ferricyanide of potassium used in its production, inasmuch as the latter contains 2Fe, and the prussian blue produced from it contains 5Fe. (Gm.)

The blue containing potassium must be regarded as a compound of 1 At. ferricyanide of potassium with 4 At. prussian blue A = $(3KCy,Fe^2Cy^3)+4(3FeCy,Fe^2Cy^3)$. (Wöhler & Völckel.) As Williamson found, in his blue (1, *β*,) a smaller quantity of potassium in proportion to the iron, it follows that this compound must have contained less ferricyanide of potassium.

Prussian blue A gives off hydrocyanic acid, even when dried in the air by the aid of heat, and thereby becomes mixed with sesquioxide of iron. (Williamson). The evolution of hydrocyanic acid is somewhat difficult to understand; the formation of ferric oxide is more easily seen, the blue A being at the same time converted into B:

$$6Fe^6Cy + 3O = 4Fe^7Cy^9 + Fe^2O^3.$$

When recently precipitated it is decomposed by aqueous caustic potash, or its carbonate, into ferrocyanide of potassium, and ferroso-ferric oxide, Fe^3O^4, which separates out. The iron in this oxide is to that in the ferrocyanide of potassium produced at the same time, as 1627 : 1077, or as 3 : 2 (Williamson):

$$3FeCy,Fe^2Cy^3 + 4KO = 2K^2FeCy^3 + Fe^3O^4.$$

By this reaction, prussian blue A is distinguished from prussian blue B; for the latter when treated with potash leaves ferric oxide.

Prussian Blue B. $C^6N^3Fe^3,2C^6N^3Fe^2+xHO=6FeCy,2Fe^2Cy^3+xHO$. *Hydrated ⅔-cyanide of Iron, Pure ordinary Prussian blue, Paris blue, Gewässertes Neunsiebentel-Cyaneisen, Eisencyanür-Cyanid, Ferrocyanideisen, reines gewöhnliches Berlinerblau, Pariserblau;* and when mixed with hydrate of alumina, white clay, &c.— *Common Prussian blue, gemeines Berlinerblau.*

Formation. 1. By precipitating a ferric salt with ferrocyanide of potassium:

$$3(2KCy,FeCy) + 2Fe^2Cl^3 = 6KCl + 3FeCy,2Fe^2Cy^3;$$

or,

$$3C^6N^3FeK^2 + 2Fe^2Cl^3 = 6KCl + C^6N^3Fe^3,2C^6N^3Fe^2;$$

or with ferric sulphate:

$$3C^6N^3FeK^2 + 2(Fe^2O^3,3SO^3) = 6(KO,SO^3) + C^6N^3Fe^3,2C^6N^3Fe^2.$$

The liquid remaining above the precipitate is neutral. (Berzelius.)—The solution of ferric oxide in organic acids, likewise yields prussian blue with ferrocyanide of potassium, even if its solution in a *volatile* organic

acid be mixed with such a quantity of ammonia as to produce a basic salt which still remains dissolved. It is only when a larger quantity of ammonia is added, sufficient to throw down all the ferric oxide, that the addition of ferrocyanide of potassium produces a dark brown-red precipitate, agreeing in composition with the residue which remains after treating prussian blue with ammonia.—If, on the contrary, a ferric salt be mixed with a sufficient quantity of a *fixed* organic acid, such as malic, tartaric, racemic, or citric acid, or of sugar, and then with such a quantity of ammonia as to make the iron-solution somewhat basic, no precipitate will be produced by ferrocyanide of potassium, or by the further addition of ammonia. Moreover, ammonia will not even turn the liquid brown, if a sufficient quantity of the fixed organic substance be present.—But on adding any acid to the ammoniacal mixture, prussian blue is immediately precipitated. Hence *Tartarus martiatus* and *Extractum martis pomatum*, which are mostly basic compounds, usually give no precipitate with ferrocyanide of potassium. (H. Rose, *Pogg.* 43, 585.)—2. By precipitating a ferroso-ferric salt with cyanide of potassium:

$$9C^2NK + 3FeCl + 2Fe^2Cl^3 = 9KCl + C^6N^3Fe^3,2C^6N^3Fe^2;$$

or,

$$9KCy + 3FeCl. + 2FeCl^3 = 9KCl + 3FeCy,2Fe^2Cy^3.$$

If the iron-salt contains a larger proportion of ferric than of ferrous salt, the presence of the latter does not appear to alter the character of the precipitate; but if the proportion of ferric salt be too small, the precipitate will probably consist of prussian blue A (pp. 436, 5).—3. By mixing hydrocyanic acid with a ferrous salt, then with excess of potash, then with excess of hydrochloric acid; or first with potash, then with a ferroso-ferric salt, and then with hydrochloric acid. In the former case, the potash, together with the hydrocyanic acid and the ferrous oxide contained in the precipitate, forms ferrocyanide of potassium; and when the rest of the precipitate is dissolved by the hydrochloric acid, the sesquichloride of iron thus produced, forms prussian blue with the ferrocyanide of potassium. In the latter case, the potash and the hydrocyanic acid first form cyanide of potassium, which then, together with the ferrous oxide contained in the ferroso-ferric salt added, forms ferrocyanide of potassium; and this again throws down prussian blue from the solution of the precipitate.—4. By immersing recently precipitated ferroso-ferric hydrate in aqueous hydrocyanic acid. If the hydrocyanic acid be added in excess, a purple solution is formed, which, on evaporation, deposits blue and purple rings; only the latter of these redissolve in water, and form a purple solution, which is converted into prussian blue by a small quantity of chlorine, and decolorized by a larger portion, after which no precipitate is produced by potash. (Vauquelin.)—5. By immersing ferrous cyanide in a solution of a ferric salt, which is thereby converted into a ferrous salt:

$$3C^6N^3Fe^3 + 2Fe^2Cl^3 = C^6N^3Fe^3,2C^6N^3Fe^2 + 6FeCl.$$

6. By mixing ferroprussic acid with a ferric salt:

$$3C^6N^3FeH^2 + 2Fe^2Cl^3 = C^6N^3Fe^3,2C^6N^3Fe^2 + 6HCl.$$

This precipitate is free from ferrocyanide of potassium.—7. By the action of air, chlorine-water, or nitric acid, on protocyanide of iron:

$$3C^6N^3Fe^3 + 3O = C^6N^3Fe^3,2C^6N^3Fe^2 + Fe^2O^3.$$

According to this equation, when oxidation takes place by the action of the air, the prussian blue produced contains ferric hydrate, which would be dissolved by nitric acid, or by a mixture of that acid with sulphuric acid; chlorine produces soluble Fe^2Cl^3.—8. By the action of air, chlorine-water, or nitric acid, on ferroprussic acid :

$$7C^6N^3FeH^2 + 2O \text{ (or } 2Cl) = C^6N^3Fe^2,2C^6N^3Fe^2 + 12C^2NH + 2HO \text{ (or } 2HCl).$$

In the reactions 7 and 8, however, $\frac{2}{3}$-cyanide of iron may likewise be formed; *e. g.*, in 8 :

$$5C^6N^3FeH^2 + O = C^6N^3Fe^2,C^6N^3Fe^2 + 9C^2NH + HO.$$

9. By the action of chlorine-water, or nitric acid, on the white compound, $C^6N^3FeK^2,C^6N^3Fe^2$ (*q. v.*).

In all cases in which the formation of prussian blue takes place in presence of a potassium-compound, the prussian blue takes up ferrocyanide of potassium in a state of intimate union, and in particular abundance when the latter is present in excess. Prussian blue containing a considerable quantity of ferrocyanide of potassium, is not soluble in the saline liquid in which it is produced; but on decanting this liquid, and washing the residue with water, the water acquires a blue colour, which becomes continually deeper as the soluble salts are removed, the water in fact dissolving the greater part of the ferrocyanide of potassium, and by means of it a large quantity of prussian blue. This is the soluble prussian blue described by Berzelius and Robiquet. With a smaller quantity of ferrocyanide of potassium, the prussian blue does not dissolve in the wash-water, but very slowly gives up to it the ferrocyanide of potassium, so that ultimately a residue is obtained, consisting of prussian blue free from potassium.

The fact that prussian blue carries ferrocyanide of potassium down with it, appears to have been first observed by Berthollet. (*Crell, Ann.* 1795, 171; *Statique Chim.* 2, 253.)—When protochloride of iron is precipitated by excess of ferrocyanide of potassium, and the liquid, together with the white precipitate ($KCy,2FeCy = C^6N^3FeK^2,C^6N^3Fe^2$), left exposed to the air till it becomes blue, the liquid remains neutral, and the blue substance obtained is prussian blue, wholly or for the most part soluble in water, but not in saline solutions; hence it must be washed with sal-ammoniac solution, and then two or three times with water. From its blue aqueous solution it is not precipitated by boiling, or by the addition of alcohol; but it is thrown down by hydrochloric acid, and by many salts, and may then be redissolved by pure water. Sulphuretted hydrogen precipitates a black substance [sulphide of iron] from the aqueous solution, and forms ferroprussic acid. (Berzelius, *Schw.* 30, 34.)

This soluble prussian blue always contains ferrocyanide of potassium. In proportion as the white precipitate turns blue on exposure to air, ferrocyanide of potassium is dissolved out of it by the watery liquid. But the quantity of potassium-salt which remains combined with the prussian blue, and renders it soluble in water, is greater in proportion as the oxidation has been less complete. Prussian blue thus constituted, still gives up ferrocyanide of potassium to pure water, even after being treated with very dilute hydrochloric acid. To obtain soluble prussian blue, the ferrous salt must be precipitated by excess of ferrocyanide of potassium; if the ferrous salt is in excess, the white precipitate, on ex-

posure to the air, is converted into insoluble prussian blue. (Robiquet, *Ann. Chim. Phys.* 44, 279.)

When prussian blue obtained by treating sesquichloride of iron with ferrocyanide of potassium, is washed with cold water, the water continually acquires a yellow or green colour, by taking up ferrocyanide of potassium; hot water is still more highly coloured by it. This effect is equally produced, whether the ferrocyanide of potassium or the sesquichloride of iron was in excess at the precipitation, excepting that the quantity of potassium contained in the precipitate is much greater in the former case than in the latter. (Gay-Lussac, *Ann. Chim. Phys.* 46, 73; 51, 370.)

When aqueous ferrocyanide of potassium is precipitated by excess of sesquichloride of iron, and the precipitate, after an hour's digestion, washed on the filter, sesquichloride of iron passes through first, then a nearly colourless liqnid, then a yellow liquid, containing ferrocyanide and ferricyanide of potassium; because the water, which contains air, decomposes part of the ferrocyanide of potassium into ferricyanide of potassium and ferric oxide, the latter remaining mixed with the prussian blue. If the precipitate be washed till the liquid which passes through no longer precipitates ferrous salts or silver salts, a residue is obtained, consisting of prussian blue free from potassium, but mixed with sesquioxide of iron, which may be dissolved out by hydrochloric acid. It appears then that prussian blue carries down ferrocyanide of potassium, even when the chloride of iron is in excess; but the potassium-salt may be completely removed by continued washing with water. (Berzelius.)

When ferrocyanide of potassium and sesquichloride of iron are mixed exactly in the proportion required to precipitate them both completely, and the precipitate is washed on a filter, a colourless liquid first passes through; then a liquid coloured yellow by ferrocyanide of potassium and a small quantity of ferricyanide: the prussian blue, after sufficient washing, is free from potassium. (Berzelius, *Pogg.* 25, 387.)

When aqueous ferrocyanide of potassium is mixed with a quantity of sesquichloride of iron not sufficient to precipitate it completely, and the precipitate washed on a filter, the liquid which first passes through is coloured yellow by ferrocyanide of potassium; after which the wash-water acquires a green, and ultimately a fine dark-blue colour.—1. The first portion of dark-blue liquid which runs through, leaves, on evaporation, a dark-blue, extractive mass, which is soluble in water, separates spontaneously from the basin, yields, when decomposed, 54·44 pts. of chloride of potassium to 100 of ferric oxide; it is probably, therefore, a compound of 1 At. ferrocyanide of potassium with 1 At. prussian blue ($C^6N^3FeK^2 + C^6N^3Fe^3, 2C^6N^3Fe^2$). The quantity of iron present is, however, less than that which this formula requires, and consequently the ferrocyanide of potassium must be somewhat in excess.—2. When the blue liquid which runs through at a later stage of the process, is evaporated to a small bulk and precipitated by alcohol, it yields a yellow filtrate, containing ferrocyanide and ferricyanide of potassium, and a blue precipitate, which yields by analysis 31·92 pts. of chloride of potassium and 100 pts. sesquioxide of iron; consequently 4K to somewhat more than 23Fe, or 2 At. ferrocyanide of potassium to 3 At. prussian blue. If a current of air be passed through such a solution at a temperature of 85°, the liquid soon becomes yellowish green, depositing ferric oxide and pure prussian blue, and forming ferricyanide of potassium.—3. If prussian blue be washed with

water, till the water which runs through is no longer dark but only pale blue, it exhibits, after being pressed between paper, the aspect of ordinary prussian blue, and yields 23·52 parts of chloride of potassium to 100 pts. of ferric oxide=2K : 16Fe; this corresponds to the combination of 1 At. ferrocyanide of potassium with 2 At. prussian blue, which requires 2K : 15Fe. (Berzelius, *Pogg.* 15, 395.)

When a warm solution of ferrocyanide of potassium is precipitated by excess of sesquichloride of iron, the mixture kept warm for some hours, and the prussian blue washed as thoroughly as possible by decantation, it still retains 1 At. K to 27 At. Fe. The greater the quantity of ferrocyanide of potassium contained in prussian blue, the paler is its colour. (Williamson.)

All commercial prussian blue, and even that which is prepared by careful chemical processes, gives up ferrocyanide of potassium to boiling water, thereby colouring it greenish yellow. (Wach, *Schw.* 51, 449.)

Preparation on the large scale.—1. By precipitating a ferric salt with less than the equivalent quantity of ferrocyanide of potassium, digesting the precipitate with the supernatant liquid, and washing it thoroughly. (Vid. *Formation* 1, also pp. 439,440, respecting the difficulty of washing all the ferrocyanide of potassium out of the precipitate.)

2. By precipitating green vitriol or any other ferrous salt with ferrocyanide of potassium, and subjecting the white precipitate KFe^2Cy^3 to the action of oxidizing agents. According to Gentele (*Polytechn. J.* 61, 452), solutions of 100 pts. ferrocyanide of potassium and 80 green vitriol are to be mixed at the ordinary temperature; the precipitate washed with water, and heated with water to the boiling point; 30 pts. of nitric acid, of 28° Bm., and 15 to 30 oil of vitriol, added; and the precipitate washed and dried by heat. It is customary also to mix it with white clay or starch.

3. Common prussian blue is prepared by the following process, which is the oldest. A solution of 1 pt. green vitriol and 2 to 4 pts. alum is precipitated by solution of ferrocyanide of potassium prepared in the manner described on page 453; and the dark-coloured precipitate, consisting of a mixture of alum, KFe^2Cy^3, and hydrated sulphide of iron, is washed with cold water, till, by the action of the air contained in the water, the sulphide of iron is converted into ferrous sulphate, and washed away, and the KFe^2Cy^3 is converted, with loss of ferrocyanide of potassium, into prussian blue. By digesting with ½ pt. dilute sulphuric acid and subsequent washing, this prussian blue may be freed, to a certain extent, from the greater part of the alumina, the basic sulphate of ferric oxide, potash-salts, and other impurities. (Turner.) To purify prussian blue, it may be dissolved in oil of vitriol, precipitated therefrom by water and washed, then digested in hydrochloric acid, and again washed with water. (*Berzelius Lehrb.*)

Properties. Dark blue, almost black, dense brittle mass, having a conchoidal, copper-coloured fracture. Inodorous, tasteless, and not poisonous. Very hygroscopic, so that, according to Berzelius, after having been dried in vacuo at ordinary temperatures, it still gives off a considerable quantity of water at 135°. Prussian blue contaminated with alumina, clay, &c., is paler in colour, and has a more earthy fracture.

Dried in vacuo.			Berzelius.
18 C	108	19·12	39·12
9 N	126	22·30	
7 Fe	196	34·69	37·90
15 HO	135	23·89	23·60
Fe^7Cy^9 + 15HO.	565	100·00	100·62

Dried in the air between 30° and 40°.			Williamson.
18 C	108	18·24	17·47
9 N	126	21·28	20·40
7 Fe	196	33·11	31·97
18 HO	162	27·37	28·19
+ 18HO	592	100·00	98·03

Berzelius, previously to analyzing the prussian blue prepared by precipitating sesquichloride of iron with ferrocyanide of potassium, dried it in vacuo over oil of vitriol at the medium temperature; another portion which was dried in vacuo at 135°, yielded 60·14 per cent. of ferric oxide when burnt; hence it may be inferred, as no cyanogen was given off at that temperature, and the ferric oxide obtained was free from potash, that the prussian blue dried at 135° contains at most 12HO. Williamson, in order to obviate completely the admixture of potassium, prepared the prussian blue which he analyzed, by precipitating sesquichloride of iron with ferroprussic acid, and dried it in the air at a temperature not exceeding 30°—40°, because, even at this temperature, the odour of hydrocyanic acid intimated incipient decomposition. He supposes that his compound contains 20HO; but for this the quantity of water given by the analysis is not sufficient. Porrett regards prussian blue as hydrated ferroprussiate of ferric oxide. (For his analysis, *vid. Schw.* 17, 301.) According to this view, prussian blue B would be $2(Fe^2O^3),3(2HFeCy^3) + 12Aq$; and prussian blue A = $FeO,Fe^2O^3,2(H^2FeCy^3) + 8Aq$. Prussian blue B may likewise be regarded as hydrated prussiate of ferroso-ferric oxide = $3(FeO,HCy),2(Fe^2O^3, 3HCy) + 9Aq$. In that case, prussian blue A would be = $3(FeO,HCy), (Fe^2O^3,3HCy) + 6Aq$.

By the combustion of dried prussian blue, Wiegler obtained 46, Thomson 48, Westrume 50, Ittner 52, Proust 55, and Berzelius, after less complete desiccation, obtained 54·46, but after drying the substance as completely as possible, from 58 to 60 per cent. of ferric oxide. These discrepancies arise from the different degrees of dryness and purity of the prussian blue.

Decompositions. Prussian blue, when subjected to *dry distillation*, yields, according to Scheele, carbonic acid, hydrocyanate of ammonia, a small quantity of oil, and a residue of iron; according to Proust, 5 vol. carbonic acid gas to 1 vol. carbonic oxide, besides hydrocyanic acid, hydrocyanate of ammonia, and carbonate of ammonia, but no oil; and leaves carboniferous iron, which takes fire on exposure to the air (according to Ittner and Berzelius, only when it is still somewhat warm). According to Ittner, prussian blue, when heated, becomes paler in colour, and ultimately white, and then gives off carbonic oxide, carbonic acid, hydrocyanic acid, and ammonia. According to Berzelius, prussian blue dried at 150°, first gives off pure water; then water with a small quantity

of hydrocyanate of ammonia; then water with a large quantity of carbonate of ammonia; at a heat somewhat below redness, the residue, which consists of sesquicarbide of iron, exhibits a bright glow. Vauquelin obtained from prussian blue, dried as completely as possible: carbonic oxide, hydrocyanic acid, hydrocyanate of ammonia, crystallized carbonate of ammonia, and a small quantity of a yellow oily deposit, soluble in aqueous potash. Thomson obtained nitrogen, a combustible gas, which he regarded as a peculiar hydrocarbon, together with water and crystallized hydrocyanate of ammonia. The residue left after two hours' ignition in a copper tube, is somewhat pyrophoric, probably from admixture of potassium, and burns with an odour like that of ammonia. (Thomson, *Ann. Phil.* 16, 217.)—Prussian blue, when carefully heated, gives off water, and assumes a pale green tint; its blue colour is therefore due to the presence of water. The gas which is afterwards given off on the application of a stronger heat, is completely absorbed by potash. Long brownish prisms sublime in the receiver, and partly dissolve in the brown liquid therein contained. These crystals have a strong ammoniacal odour, do not yield prussian blue with ferric salts after neutralization with nitric acid [why was not a ferroso-ferric salt used?], but form, with silver-solution, a precipitate which exhibits the characters of carbazotide of silver, isomeric with the cyanide (*vid. Cyanide of Silver*). The crystals cannot, therefore, consist of hydrocyanate of ammonia [?], which, moreover, crystallizes in cubes, and is more volatile. The brown liquid in the receiver, which retains a portion of these crystals in solution, exhibits the same reactions as the crystals themselves, turns turmeric brown, and throws down carbonate of baryta from baryta-water. Carbonate of ammonia likewise passes over. The residue, if left in the retort till perfectly cold, does not take fire spontaneously on coming in contact with the air, but while still warm it burns away rapidly in the air, like gunpowder. It may be regarded as paracyanogen mixed with still undecomposed prussian blue, which remains undissolved on digestion with dilute nitric acid. The solution of the residue in oil of vitriol, yields, with water, a precipitate of paracyanogen, which, however, is not of so pure a brown colour as pure paracyanogen. (Thaulow, *J. pr. Chem.* 31, 230.)—2. Thoroughly dried prussian blue takes fire when gently *heated in contact with air*, according to Thomson, at 204°, and burns away like tinder, giving off hydrocyanate of ammonia (Vauquelin), or carbonate of ammonia (Berzelius), and being converted into ferric oxide. If the prussian blue contains ferrocyanide of potassium, cyanate of potash is also found in the residue. (*Berzelius Lehrb.*)—Prussian blue, even when gently heated in the air, gives off cyanogen in the form of hydrocyanic acid, and becomes contaminated with ferric oxide (Williamson):

$$Fe^7Cy^9 + 3HO = 3HCy + Fe^2O^3 + Fe^5Cy^6.$$

Water containing air decomposes prussian blue very slowly, forming paracyanogen and ferric oxide; but water free from air has no effect on it, even in very large quantity. (Berzelius, *Pogg.* 25, 388.)—1 gramme of prussian blue, after being washed with water for 3 weeks, during which time 40 pounds of water are passed through it, appears quite unaltered, excepting that it has acquired a violet tinge; the apex of the filter which does not lie close to the funnel, and is consequently exposed to the air, is found to be turned brown, not from formation of ferric oxide, but from paracyanogen; 1 pt. of recently precipitated prussian blue digested for three weeks with 1300 pts. of water, and in contact with the air, the

water being replaced as it evaporates, remains unaltered till the third week, when it exhibits a greenish colour. (Berzelius.)—3. *Nitric acid* and *oil of vitriol*, heated with prussian blue, decompose it by giving up oxygen to it. — 4. *Chlorine-water* converts it into a green compound [probably that described by Pelouze, p. 446], which turns blue in contact with protochloride of iron or protochoride of tin. The compound retains its green colour after being subjected to pressure, but is turned blue again, both by drying (even without the aid of heat) and by washing with water. (*Berzelius Lehrb.*) — Aqueous chloride of lime, heated with prussian blue, quickly decomposes it with effervescence and formation of a brown-red neutral liquid, which gives a blue precipitate with ferrous salts [probably, therefore, contains ferricyanide of potassium], and when evaporated, yields crystals of chlorate of potash formed from the potassium in the prussian blue. (Liebig, *Pogg.* 15, 571.) — 5. Aqueous solution of *nitrate of silver* decomposes prussian blue, imperfectly at ordinary temperatures, perfectly with the aid of heat, giving off nitric oxide, and forming ferric nitrate which dissolves, and cyanide of silver mixed with ferric oxide. (Wöhler, *Pogg.* 1, 235.) — 6. When prussian blue is boiled with *minium*, there is formed from the potassium in the prussian blue, a solution of ferricyanide of potassium free from lead, and a mixture of ferrocyanide of lead and ferric oxide, together with excess of minium. (Berzelius, *Jahresber.* 10, 145.) — 7. Prussian blue digested with *mercuric oxide* and water, yields cyanide of mercury, which dissolves in a few hours, even at ordinary temperatures, and ferroso-ferric oxide:

$$Fe^7Cy^9 + 9HgO = 9HgCy + (3FeO,2Fe^2O^3).$$

According to Vauquelin, the ferroso-ferric oxide thus formed retains cyanogen, and therefore when dissolved in acids leaves a small quantity of prussian blue.—8. The *alkalis* and magnesia, in presence of water, decompose prussian blue more quickly with the aid of heat, sometimes however but imperfectly, forming a compound of 2 At. cyanide of the alkali-metal and 1 At. protocyanide of iron, and leaving a residue of ferric oxide:

$$Fe^7Cy^9 + 6KO = 3(K^2FeCy^3) + 2Fe^3O^3.$$

Potash exerts the most powerful decomposing action, and leaves ferric oxide free from cyanogen. (Proust, Ittner, Berzelius.) In this case, 100 pts. of prussian blue, if they contain 15 At. water (p. 442), must yield 28·32 ferric oxide and 112·25 crystallized ferrocyanide of potassium ($565 : 2 \cdot 80 = 100 : x$; and $565 : 3 \cdot 211{\cdot}4 = 100 : x$). Thomson (*Ann. Phil.* 15, 392) obtained from prussian blue dried at 66°, 37·8 pts. of ferric oxide and 96·5 ferrocyanide of potassium; perhaps his prussian blue had been previously mixed with ferric oxide by decomposition in the air.—*Ammonia*, according to Berzelius, decomposes prussian blue imperfectly, and leaves a greyish brown basic compound, which again forms prussian blue when treated with acids; *lime* also, when boiled with prussian blue, leaves a similar basic compound, but of a light yellow colour.—*Carbonate of potash* or *soda* acts less strongly than the caustic alkali. Bicarbonate of potash, according to Grotthuss (*Schw.* 30, 72), gradually blackens prussian blue, depositing white ferrous carbonate, and forming a liquid from which acids immediately precipitate prussian blue [perhaps because, in addition to ferrocyanide of potassium, it contains ferric oxide dissolved in carbonate of potash]. A hot aqueous solution of *carbonate of ammonia* separates sesquioxide of iron. (Wittstein.)—*Carbo-*

nate of lime likewise decomposes prussian blue, when boiled with it in water (Scheele, Guyton-Morveau); also the *carbonates of baryta, strontia, and lime,* and even *carbonate of magnesia.* (*Kastn. Arch.* 20, 316.) Bette, on the contrary (*Ann. Pharm.* 22, 148), denies this decomposibility of prussian blue by the carbonates of baryta and strontia.—9. Prussian blue is not attacked by cold *hydrochloric acid* in small quantity; when heated with that acid, it becomes decolorized, but afterwards recovers its blue colour, evolves a small quantity of hydrocyanic acid, and gives up ferric oxide to the hydrochloric acid; it thereby acquires a lighter blue colour, and becomes looser in texture, and when afterwards treated with potash, leaves hydrated ferric oxide, not brown but yellow. (Robiquet.) By continued cold digestion with excess of highly concentrated hydrochloric acid, it becomes first green and then yellowish, from loss of ferric oxide; and if the residue be washed with the strong hydrochloric acid as long as that acid continues to dissolve ferric oxide, the ultimate residue will consist of ferroprussic acid (Robiquet):

$$Fe^7Cy^9 + 6HCl = 2Fe^2Cl^3 + 3H^2FeCy^3.$$

If the hydrochloric acid solution be diluted with water before separating it from the ferroprussic acid, the prussian blue will be reproduced. (Robiquet.)—10. Aqueous solution of *sulphuretted hydrogen* gradually converts prussian blue in closed vessels into white protocyanide of iron (Proust), which compound, according to Robiquet, is deposited in yellow crystals. According to Berzelius, prussian blue immersed in sulphuretted hydrogen-water first turns pale blue and then dirty white; the liquid contains ferroprussic acid: the white substance is a mixture of ferrous cyanide and sulphur; it recovers its blue colour on exposure to the air, being thereby partly converted into soluble prussian blue; but both the portion soluble in water and the insoluble portion are blackened by sulphuretted hydrogen. The equation is probably:

$$Fe^7Cy^9 + 2HS = H^2FeCy^3 + 6FeCy + 2S;$$

or,

$$C^6N^3Fe^3 + 2C^6N^3Fe^3 + 2HS = C^6N^3FeH^2 + 2C^6N^3Fe^3 + 2S.$$

11. *Dichloride of copper* dissolved in hydrochloric acid immediately decolorizes recently precipitated prussian blue. (Proust, *A. Gehl.* 6, 578.) 12. *Iron* or *tin* filings placed in contact with prussian blue under water in close vessels, withdraw part of its cyanogen, and convert it into white protocyanide of iron.—13. When prussian blue is boiled with a *polysulphide of potassium,* sulphocyanide of potassium [and sulphide of iron?] is formed (Porrett), perhaps in this manner:

$$Fe^7Cy^9 + 9KS^3 = 9KCyS^2 + Fe^7S^9.$$

Combinations. a. Prussian blue immersed in cold *oil of vitriol* turns white, without evolving hydrocyanic acid or giving up iron; the addition of water, alcohol, or ether, restores the colour, even without contact of air. (Robiquet.) The white pasty mass does not dissolve in excess of oil of vitriol; when dried in vacuo on a porous tile, it leaves a white amorphous powder, the *Sulphate of Prussian blue,* which by contact with water is immediately resolved into prussian blue and dilute sulphuric acid. (Berzelius.)

b. With Ammonia.—*Ammoniacal Prussian blue.*—$3(FeCy,NH^3,HO) + 2(Fe^2Cy^3) + 9HO$. This compound is produced at the commencement of the action of ammonia on prussian blue, but cannot in that manner be

obtained free from ferric oxide. To prepare it, a solution of harpsichord-wire in hydrochloric acid is saturated with ammonia; the liquid [which contains protochloride of iron and ammonium, together with excess of ammonia (V., 263)] filtered into an aqueous solution of ferrocyanide of potassium into which the beak of the funnel dips; and the white precipitate, after being left to turn blue in the air, is digested for some hours at 60°—80°, with normal tartrate of ammonia, to dissolve the ferric oxide formed during the blueing; afterwards washed with water, and dried in the hot-air chamber. The first product formed is white ammoniacal cyanide of iron:

$$3K^2FeCy^3 + 6FeCl + 9NH^3 + 9HO = 6KCl + 9(FeCy,NH^3,HO);$$

and this, when exposed to the air, takes up 3O, gives up $6NH^3$, and is converted into ammoniacal prussian blue and ferric oxide (Monthiers):

$$9(FeCy,NH^3,HO) + 3O = Fe^7Cy^9,3NH^3,9HO + 6NH^3 + Fe^2O^3.$$

Blue powder with a tinge of violet.

				Monthiers.
18 C	108	19·22		19·2
12 N	168	29·89		30·1
7 Fe	196	34·88		35·0
18 H	19	3·20		3·6
9 O	72	12·81		12·1
$Fe^7Cy^9,3NH^3,9HO$	562	100·00		100·0

The compound begins to give off hydrocyanic acid at 100°, but retains its colour up to 160°, below which temperature no ammonia is evolved. When heated to redness in an open vessel, it leaves ferric oxide free from potash. By mercuric oxide and water it is decomposed in a few days at ordinary temperatures, but immediately on the application of heat. Aqueous fixed alkalis immediately cause an evolution of ammonia, and separate ferric oxide. Aqueous ammonia exerts a very slow decomposing action, particularly slow when it is dilute. Nitric acid, aqua-regia, hydrochloric and sulphuric acid, act upon this compound as upon prussian blue; but the ammoniacal compound withstands their action longer than pure prussian blue. It is likewise insoluble in normal tartrate of ammonia, in which respect it differs materially from pure prussian blue. (Monthiers, *N. J. Pharm.* 9, 26; also *J. pr. Chem.* 38, 173; abstr. *Compt. rend.* 21, 435.)

With $\frac{1}{6}$th of oxalic acid (dissolved in water) prussian blue forms a beautiful blue solution, which serves for a blue ink (vid. *Oxalic acid*). It dissolves in aqueous normal tartrate of ammonia, forming a solution of a beautiful violet colour (*q.v.*).

Prussian blue is insoluble in water, alcohol, ether, oils, and dilute acids.

Prussian Green. $C^6N^3Fe^3,3C^6N^3Fe^3 + 12HO = FeCy^6, Fe^2Cy^3 + 4HO$.—*Hydrated Four-thirds Cyanide of Iron, Green Cyanide of Iron, Berlinergrün, gewassertas Vierdrittelcyaneisen, grunes Cyaneisen, mittleres Cyaneisen.*—Formerly regarded as chlorocyanide of iron; its true nature was first recognized by Pelouze (*Ann. Chim. Phys.* 69, 40; also *J. Pharm.* 24, 545; abstr. *Pogg.* 48, 222; abstr. *J. pr. Chem.* 16, 104).

Formed by the action of excess of chlorine upon aqueous ferrocyanide or ferricyanide of potassium; and by leaving ferrocyanide of potassium

for some time in contact with aqueous acids, especially at high temperatures. (Pelouze.)

Chlorine gas is passed in excess through an aqueous solution of ferrocyanide or ferricyanide of potassium; the resulting wine-red solution, which has the penetrating odour of chloride of cyanogen, exposed to the air, or better, heated to the boiling point; the precipitated green powder collected, and boiled with 8 to 10 parts of strong hydrochloric acid, which dissolves any accidentally admixed ferric oxide and decomposes the prussian blue, till a filtered sample no longer turns blue on being mixed with water. The residue is then washed with water, and dried in vacuo. (Pelouze.)

Green, light, tasteless powder.

Calculation, according to Pelouze.

8 C	48	.....	21·43
4 N	56	.....	25·00
3 Fe	84	.....	37·50
4 HO	36	.....	16·07
	224		100·00

The quantity of water in prussian green dried in vacuo is exactly sufficient to form ferroso-ferric hydrocyanate, or hydrocyanate of magnetic oxide of iron = $FeO,HCy + Fe^2O^3,3HCy$. (Pelouze.)

This compound gives off cyanogen at 180°, together with a small quantity of hydrocyanic acid, and is converted in a few minutes into prussian blue of a deep violet colour. When exposed for some time to the air, it gives off cyanogen, and is converted into prussian blue. It is decomposed by strong hydrochloric acid, but not so readily as prussian blue, many hours' boiling being required to produce complete decomposition; the liquid then contains protochloride and sesquichloride of iron. Chlorine also decomposes prussian green less easily than prussian blue. Potash-ley immediately converts it into ferric oxide, and a liquid containing both ferrocyanide and ferricyanide of potassium (Pelouze):

$$6(FeCy,Fe^2Cy^3) + 15KO = 6(2KCy,FeCy) + 3KCy,Fe^2Cy^3 + 5Fe^2O^3;$$

or,

$$2(C^6N^3Fe^2 + 3C^6N^3Fe) + 15KO = 6C^6N^3FeK^2 + C^6N^3K^3,C^6N^3Fe^2 + 5Fe^2O^3.$$

To this compound discovered by Pelouze, the following bodies are likewise very probably related:

1. On passing chlorine gas through aqueous hydrocyanic acid, then adding potash, afterwards an iron-salt, and concentrating the liquid to a certain point, a green precipitate is obtained, which is turned blue by iron, green vitriol, or sulphurous acid. It is therefore oxidized hydrocyanate of iron. (Berthollet, *Statique chim.* 2, 263.) To produce the green precipitate, the prussic acid saturated with chlorine must be mixed, first with an iron-salt, then with potash, and afterwards with an acid; if the potash be added before the iron, no green precipitate will be formed. (Gay-Lussac.) Bromide of cyanogen acts like the chloride. Iodide of cyanogen, on the contrary, forms a green precipitate, whether it be mixed, first with green vitriol, then with potash, and then with acid, or first with potash, then with green vitriol, and then with acid. (Serullas, *Ann. Chim. Phys.* 35, 346.)

2. According to Jonas (*N. Br. Arch.* 23, 33), a green precipitate is obtained by passing chlorine in excess through an aqueous solution of

ferrocyanide of potassium, and precipitating ferric salts with the dark greenish yellow liquid thus produced.

3. On boiling the blue substance, $K^2Fe^8Cy^{12},9HO$ (*vid. infra*), with nitric acid, a dark green product is formed, containing 2·24 per cent. K, 35·85 Fe, 23·25 C, and 13·45 water. It gradually turns blue when exposed to light. Solution of potash separates hydrated ferric oxide from it, and forms a brown-red solution, which gives blue precipitates both with ferric and with ferrous salts, and when boiled, turns paler, and yields hydrated ferric oxide,—a character which is likewise exhibited by Pelouze's compound. (Williamson.)

4. Recently precipitated prussian blue acquires a dark bluish-green colour by contact with aqueous sesquichloride of iron. (Döbereiner.)

But the following green compound is probably different from this: There are green modifications of ferrocyanide of ammonium and ferrocyanide of potassium, and when their aqueous solutions are evaporated, a green powder is thrown down. The same compound is obtained when hydrocyanate of ammonia, which has decomposed and turned brown by keeping, is precipitated by a ferric salt. The green precipitate subjected to dry distillation, exhales a strong odour of empyreumatic oil, and gives off carbonate of ammonia. It is turned blue by sulphuric or hydrochloric acid, but not by deoxidizing substances. (Berzelius.) [Is the change of the blue colour to green in the preparation of this compound, effected by the brown matter formed in it from decomposition of the hydrocyanate of ammonia?]

Sesquicyanide of Iron or Ferric Cyanide.—$C^6N^3Fe^2 = Fe^2Cy^3$.—*Anderthalb-Cyaneisen, Eisencyanid.*

1. Aqueous solution of ferricyanide of potassium forms, with sesquichloride of iron, a clear dark-brown mixture, which may be regarded as a mixture of chloride of potassium and sesquicyanide of iron:

$$K^3Fe^2Cy^6 + Fe^2Cl^3 = 3KCl + 2Fe^2Cy^3.$$

The solution, if somewhat concentrated, gradually becomes covered—more quickly if gently heated—with a film of prussian blue, giving off cyanogen or chlorine gas, accordingly as it contains ferricyanide of potassium or sesquichloride of iron in excess. Sulphuretted hydrogen, sulphurous acid, and other deoxidizing agents (which will be mentioned in connection with ferricyanide of potassium), instantly throw down from the brown liquid a large quantity of prussian blue. (Gm. *Schw.* 34, 344.) In this reaction, ferroprussic acid appears likewise to be formed (p. 4).

2. Aqueous ferricyanide of potassium is added to aqueous sesquifluoride of iron and silicium (V., 288) till all the potassium is thrown down in the form of silico-fluoride of potassium:

$$3KCy,Fe^2Cy^3 + Fe^2F^6,3SiF^6 = 2Fe^2Cy^3 + 3(KF,SiF^2).$$

The liquid decanted from the potash-salt has a dark brown-yellow colour and harsh taste. It may be concentrated by spontaneous evaporation, but in drying up, it changes almost entirely into prussian blue. (*Berzelius Lehrb.*)

Sesquicyanide of iron is not formed by mixing cyanide of potassium with sesquichloride of iron; the products thereby produced are chloride of potassium, free hydrocyanic acid, and precipitated ferric hydrate; the latter, however, if left for some time in the liquid, is deoxidized (accord-

ing to Ittner) by the hydrocyanic acid, and on subsequently dissolving it in hydrochloric acid, there remains a small quantity of prussian blue. According to Haidlen & Fresenius, the liquid above the precipitate contains a small quantity of ferrocyanide of potassium.

	Calculation.		
6 C	36	.....	26·86
3 N	42	.....	31·34
2 Fe	56	.....	41·80
Fe^2Cy^3	134	.....	100·00

Ferric cyanide forms with the cyanides of other metals, a class of compounds which may be called FERRICYANIDES or FERRIDCYANIDES (*Anderthalbcyaneisen-Cyanmetalle, Ferridcyanidé*). The two kinds of prussian blue, as well as prussian green, may also be included in this class of bodies. Compounds of ferric cyanide with the cyanides of the alkali-metals, contain 3 At. cyanide of alkali-metal to 1 At. ferric cyanide; they are yellowish red, and form yellow solutions in water. Their aqueous solutions form, with the salts of the heavy metals, precipitates which are compounds of ferric cyanide with the cyanides of other heavy metals, *e.g.*:

$$3KCy,Fe^2Cy^3 + 3(PbO,SO^3) = 3PbCy,Fe^2Cy^3 + 3(KO,SO^3).$$

Hydroferricyanic or Ferriprussic Acid. $C^6N^3H^3,C^6N^3Fe^3 = 3HCy,Fe^2Cy^3$.

Ter-hydrocyanate of Ferric oxide, Red ferroprussic acid; Dreifach blausaures Eisenoxyd, Ferridcyanwasserstoffsäure (Liebig); *Wasserstoffeisencyanid* (Berzelius); *rothe Eisenblausäure.*

1. Ferricyanide of lead is decomposed by trituration with dilute sulphuric acid, the proportion of which is so adjusted that the liquid shall neither be clouded by chloride of barium nor precipitated red-brown by sulphuretted hydrogen. The decanted deep yellow solution forms, when carefully heated, brownish needles, which redden litmus strongly, and have a rough sourish taste. If the liquid be evaporated to dryness at a somewhat stronger heat, there remains a residue which, when water is poured upon it, decrepitates, swells up, and is reduced to a dark brown powder, without giving up much soluble matter to the water. The aqueous solution of the undecomposed compound is brown when saturated, bright yellow when dilute. When left to itself, or when heated, it deposits a pale prussian blue of crystalline aspect; paper saturated with the solution acquires a green colour, from deposition of prussian blue. The solution precipitates prussian blue from ferrous salts, and imparts a brighter brown colour to sesquichloride of iron (by formation of sesquicyanide?). (Gm. *Schw.* 34, 343.)

2. Berzelius (*Lehrb.*) throws down the greater part of the potassium from aqueous ferricyanide of potassium by adding a quantity of hydrofluosilicic acid not sufficient to precipitate the whole; then adds alcohol to precipitate the undecomposed portion of the ferricyanide; and leaves the filtrate to evaporate in vacuo over oil of vitriol.

3. F. & E. Rodgers (*Phil. Mag. J.* 4, 93) decompose the saturated aqueous solution of 329·6 parts (1 At.) of ferricyanide of potassium with 450 pts. (3 At.) of tartaric acid dissolved in alcohol. It is advisable to have the ferricyanide of potassium a little in excess rather than the tartaric

acid, because the former is precipitated by the alcohol. The potash is completely precipitated in the form of cream of tartar. The decanted yellow acid liquid is decomposed by exposure to light, and acquires a dark green colour.

4. L. Posselt (*Ann. Pharm.* 42, 176) proceeds in the same manner as Gm. According to his statement, the red-brown solution deposits, after standing for some time, a light-brown crystalline powder; it is very easily reduced by sulphurous acid, by zinc with hydrochloric acid, and by heating with cyanide of potassium; by boiling, it is completely resolved into a dark-green powder and hydrocyanic acid, the latter escaping. Posselt assigns to this green precipitate, in accordance with his own analysis, the formula $Fe^2Cy^3,3HO$, from which it would follow that in the decomposition which takes place on boiling, 3HCy simply goes off, and Fe^2Cy remains in combination with 3HO. [But a green powder which sustains a boiling heat without decomposition can scarcely be regarded as Fe^2Cy^3, which at least, according to p. 448, is a brown, soluble, easily decomposible compound. Posselt's green powder is perhaps identical with Pelouze's green compound, $Fe^3Cy^4,4HO$, and is formed from Fe^2Cy^3 by boiling, with evolution of cyanogen: $3Fe^2Cy^3 - Cy = 2Fe^3Cy^4$.]

12 C	72	.....	33·49
6 N	84	.....	39·07
3 H	3	.....	1·40
2 Fe	56	.....	26·04
$3HCy,Fe^2Cy^3$	215	.....	100·00

Ferrocyanide of Ammonium, or Hydrocyanate of Ferrous Oxide and Ammonia.

$C^6N^3Fe(NH^4)^3,3HO = 2NH^4Cy,FeCy + 3HO = 2(NH^3,HCy) + (FeO,HCy)$.

Einfach Cyaneisenammonium, Ammonium, Eisen-Cyanür, flüchtiges Blutlaugensalz.

1. Prussian blue is digested with aqueous ammonia, the solution filtered, and the excess of ammonia left to volatilize in the air. (Scheele.) This process yields but a small product (according to Bunsen, nothing at all), and if the prussian blue contains ferrocyanide of potassium, the same impurity will be found in the product. (Gay-Lussac, *Ann. Chim. Phys.* 46, 79.) The author likewise obtained nothing but ferrocyanide of potassium by this process. — 2. Ferrocyanide of lead is digested with carbonate of ammonia, and the salt which would be decomposed by evaporation, precipitated by alcohol. (Berzelius.) Bette (*Ann. Pharm.* 23, 120) obtained, by this precipitation by alcohol, no crystals, but a syrup which settled at the bottom of the liquid; he therefore thinks it better to evaporate the aqueous solution. — 3. This compound is also formed, by saturating ferroprussic acid with ammonia. (Berzelius.) The very pale yellow, transparent crystals are square-based octohedrons, isomorphous with ferrocyanide of potassium (*Fig.* 25; $e : e'' = 136° 45'$). (Bunsen.) Smells of hydrocyanic acid and ammonia; its taste is biting and bitter. The crystals, if heated out of contact of air, after being dried in vacuo, give off water and hydrocyanate of ammonia, acquire a greenish colour, from formation of a small quantity of prussian blue, and leave greyish yellow ferrous cyanide, which, when further heated, exhibits the decompositions already mentioned as belonging to that compound. (Berzelius.)

The dry crystals are permanent in the air (Bunsen); they acquire a blue colour when kept for some time in vessels containing air, more quickly when heated to 40°. (Berzelius.) The aqueous solution gives off hydrocyanate of ammonia when boiled, and if the air has access to it, deposits prussian blue. (Scheele, *Opusc.* 2, 158.) The solution mixed with chloride of sodium and left to evaporate freely, yields ferrocyanide of sodium and a compound of ferrocyanide of ammonium with sal-ammoniac. (Bunsen.) The salt dissolves very readily in water, not in alcohol.

	Crystallized.				Bunsen.
2 NH^4Cy	88	....	52·07	.....	50·92
FeCy	54	....	31·95	.....	31·93
2 HO	27	....	15·98	.....	17·15
$C^6N^3FeAm^2 + 3Aq$	169	....	100·00	.....	100·00

Green Hydrocyanate of Ferrous Oxide and Ammonia.—Berzelius, by digesting prussian blue with ammonia, obtained, in addition to the yellow compound just described, a green salt, which separated in green needles from the solution after it had been evaporated to the consistence of a syrup; its solution became brown when mixed with excess of ammonia, but recovered its green colour when the ammonia was evaporated, and then deposited the green powder already described (p. 448), the rest of the liquid retaining in solution a portion of the green salt still unaltered.

Bromo-ferrocyanide of Ammonium.—$(2NH^4Cy,FeCy) + NH^4Br$. — Separates easily from the mixed aqueous solution of the two salts, in wine-yellow, shining, acute rhombohedrons, permanent in the air (*Fig.* 151); often with truncated lateral edges; $r^1 : r^3$ or $r^5 = 105° 15'$; $r^3 : r^5 = 75° 30'$ nearly. They decrepitate when heated, and leave ferric oxide after being ignited in the air. They dissolve very readily in water, and their solution is decomposed by boiling. (K. Himly & R. Bunsen, *Pogg.* 38, 208.)

Chloro-ferrocyanide of Ammonium. — $(2NH^4Cy,FeCy) + NH^4Cl$. — 1. Formed by digesting prussian blue with an aqueous solution of sal-ammoniac and ammonia. — 2. By leaving an aqueous mixture of ferrocyanide of ammonium and sal-ammoniac to crystallize.—The crystals obtained by (1) and (2) have a green colour, proceeding from admixed cyanide of iron; hence the following method is preferable. — 3. By boiling 1 pt. of ferrocyanide of potassium with 1 pt. sal-ammoniac and 6 pts. water, filtering from the cyanide of iron, and cooling the liquid very slowly. The required compound crystallizes out first, afterwards free sal-ammoniac. The crystals of the former salt, after drying, are separated mechanically from those of the sal-ammoniac, then dissolved in water, and brought to the crystallizing point by evaporation in vacuo over oil of vitriol.

Wine-yellow, transparent crystals, having a glassy lustre and permanent in the air; sometimes acute rhombohedrons agreeing in form with those of the preceding compound, sometimes more obtuse rhombohedrons, arising from truncation of the terminal edges of the more acute rhombs. Frequently also with P-face and the σ-faces of the six-sided prism. Angles of the more acute rhomb: $r' : r^3$ or $r^5 = 105° 50'$; $r^3 : r^5 = 75° 38'$ nearly. Angles of the more obtuse rhomb: $r' : r^3$ or $r^5 = 82° 54'$; $r^3 : r^5 = 96° 52'$ nearly.—The crystals decrepitate violently, and leave ferric oxide when ignited in contact with air.—Oil of vitriol disengages hydrochloric acid from them; dissolves the residue at a gentle heat, and

then, near its boiling-point, exerts a decomposing action on the cyanogen-compound. The aqueous solution of the salt is resolved, by boiling, into cyanide of ammonium which escapes, cyanide of iron which is precipitated, and sal-ammoniac which remains in solution. It precipitates metallic solutions in the same manner as ferrocyanide of potassium, the sal-ammoniac remaining in solution. The salt dissolves very readily in water. (Bunsen, *Pogg.* 36, 409.)

	Crystallized.				
$2\,NH^4Cy$	88·0	....	39·57	....	38·01
$FeCy$	54·0	....	24·28	....	25·08
NH^4Cl	53·4	....	24·01	....	25·66
$3\,HO$	27·0	....	12·14		
$(2NH^4Cy,FeCy),NH^4Cl,3HO$	222·4	....	100·00		

Ferricyanide of Ammonium or *Hydrocyanate of Ferric Oxide and Ammonia.* — $C^6N^3(NH^4)^3,C^6N^3Fe^3 + 6Aq = 3NH^4Cy,Fe^3Cy^3 + 6Aq$. — Obtained by passing chlorine gas through an aqueous solution of ferrocyanide of ammonium, till the liquid no longer forms a blue precipitate with ferric salts (which are quite free from ferrous salts); evaporating the solution to a certain point; mixing it with strong alcohol; leaving the filtrate to evaporate spontaneously; separating the resulting red prisms from the yellow cubes of sal-ammoniac which rest upon them; redissolving them in water; and leaving the salt to crystallize by spontaneous evaporation. (Bette, *Ann. Pharm.* 23, 117.)

When chlorine gas is passed through aqueous ferrocyanide of ammonium, the liquid effervesces, and white fumes of sal-ammoniac are immediately formed; it then deposits a red powder, becomes dark red as the effervescence diminishes, and loses the property of forming a blue precipitate with ferric salts. But on evaporation, even below 40°, or even after being kept for some time, the liquid decomposes, giving off cyanogen and depositing a large quantity of prussian blue. The liquid filtered from this deposit produces no blue colour with either ferric or ferrous salts, and contains nothing but sal-ammoniac and chloride of iron. (Kramer, *J. Pharm.* 15, 98.) Kramer probably allowed the chlorine to act in too great quantity.

This salt forms short, ruby-coloured, oblique rhombic prisms. It is permanent in the air. (Bette.)

The crystals, when kept for 6 hours at 100°, lose only 2 per cent. The matter thus removed consists partly of ammonia, so that, on redissolving the residue, a small quantity of prussian blue remains behind. At a higher temperature the crystals decrepitate, and leave a mixture of charcoal and oxidized iron. They dissolve readily in water. The solution, after a considerable time, deposits a precipitate; it is not precipitated by alcohol. (Bette.)

				Or:			
$3\,NH^4$	54	16·88	16·96	$3\,NH^3$	51		15·94
$2\,Fe$	56	17·50	16·90	Fe^2O^3	80		25·00
$6\,Cy$	156	48·75	49·33	$6\,HCy$	162		50·62
$6\,HO$	54	16·87	16·81	$3\,HO$	27		8·44
	320	100·00	100·00		320		100·00

Ferrocyanide of Potassium. $K^2FeCy^3=C^6N^3FeK^2$.

Prussiate of Potash, Ferroprussiate of Potash, Yellow Prussiate of Potash; Einfach-Cyaneisenkalium, weisses Cyaneisenkalium, eisenblausaures Kali, phlogistisirtes Alkali, dreifach blausaures Kali, blausaures Eisenkali, blausaures Eisenoxydulkali Ferrocyankalium, Kaliumeisencyanür.

Formation.—Ferrocyanide of potassium is formed on bringing together the following substances: Protocyanide of iron with aqueous cyanide of potassium.—Ferroprussic acid with pure potash or carbonate of potash. —Hydrated ferrous oxide with cyanide of potassium, potash being formed at the same time:

$$3KCy + FeO = K^2FeCy^3 + KO.$$

Protocyanide of iron with aqueous potash, ferrous oxide being likewise separated:

$$3FeCy + 2KO = K^2FeCy^3 + 2FeO.$$

Prussian blue A or B with aqueous potash, ferroso-ferric or ferric oxide being simultaneously separated.—By bringing compounds of ferrous cyanide with various other metallic cyanides, in contact with aqueous potash; *e.g.*:

$$Cu^2FeCy^3 + 2KO = K^2FeCy^3 + 2CuO.$$

Iron with aqueous cyanide of potassium in a vessel from which air is excluded, hydrogen gas being evolved at the same time. The action is slow at ordinary temperatures, but takes place more quickly at boiling heat (Geiger, *Ann. Pharm.* 1, 60):

$$Fe + 3KCy + HO = K^2FeCy^3 + KO + H.$$

If the air has access to the mixture, the potash is oxidized, not by the O of the HO but by that of the air, which is rapidly absorbed. (Liebig.) Sulphide of iron with aqueous cyanide of potassium, sulphide of potassium being likewise formed (Liebig, *Ann. Pharm.* 38, 20):

$$FeS + 3KCy = K^2FeCy^3 + KS.$$

According to Haidlen & Fresenius (*Ann. Pharm.* 43, 133), recently precipitated protosulphide of iron dissolves but very slowly in warm aqueous cyanide of potassium, but quickly on the addition of potash.—A ferrous salt with aqueous cyanide of potassium: the reddish yellow precipitate at first produced dissolves in the excess of cyanide of potassium when heated, forming a solution of ferrocyanide of potassium (Liebig):

$$FeO,SO^3 + 3KCy = K^2FeCy^3 + KO,SO^3.$$

Preparation on the large scale.—75 pounds of crude potash are introduced into a pear-shaped cast-iron flask placed somewhat aslant (or 3 times that quantity into a cast-iron dish 5 feet long, $3\frac{1}{2}$ feet wide, and from 4 to 6 inches deep), and heated above the melting-point in a reverberatory furnace; and 65 pounds of charcoal from blood, horns, hoofs, cuttings of skin or leather, together with 2 pounds of iron filings or smithy scales (or treble these quantities) gradually added, first in small and then in larger portions. Strong intumescence takes place, especially at first, from escape of carbonic acid and combustible vapours and gases which burn with flame. The above-named animal substances may also be used in the uncharred state; but they produce more gas and vapour, and therefore cool the carbonate of potash more quickly. The ignition is continued till the mass is brought into a state of quiet, viscid fusion, and

gives off white fumes [of cyanide of potassium?], after which it is taken out. The fused mass thus obtained from 75 pounds of crude potash, amounts to 95—98 pounds, and yields from 18 to 22 pounds of crystallized ferrocyanide of potassium. To obtain the crystallized salt, the fused mass, after cooling, is digested in water which is stirred and moderately warmed, till the solution exhibits a density of 1·148; it is then left to subside, and decanted, and the undissolved residue twice treated with water in a similar manner, the last time however at a boiling heat. It is useful to add ferrous acetate to the mixture of the fused mass and water, till the evolution of ammonia diminishes, because the cyanide of potassium not yet combined with cyanide of iron is thereby converted into ferrocyanide of potassium and acetate of potash. The undissolved residue is again washed with water, and the weak solution thus obtained is used to dissolve fresh portions of the fused mass. The lixiviated charcoal, (called *Blutlaugenkohle* in Germany), which is distinguished by great decolorizing power, is used for decolorizing and for manure.—The mixture of the three solutions obtained as above is completely clarified by subsidence and decantation; evaporated at 95° to a density not exceeding 1·27; run off into the crystallizing vessel; and after some days the mother-liquid is separated from the crystals then formed, evaporated to the density of 1·49, and stirred till it is cold. The mother-liquor which runs off from the last formed crystals is evaporated, and used instead of potash for the next fusion. The first and second crops of crystals are purified by recrystallization. The above is taken from the descriptions of Gentele (*Polytechn. J.* 61, 289), and of Hoffelmeyer & Prückner, collated by Mohr (*Ann. Pharm.* 23, 160).

To 10 pts. of crude potash it is usual to add 10 pts. of uncharred, or 8 pts. of charred animal matter, mixed with 3 or 4 parts of iron filings. The formation of cyanide of potassium, by fusing animal substances with carbonate of potash, takes place in two ways: 1. The carbonate of ammonia which rises from the mixture forms cyanide of potassium with the fused mixture of charcoal and carbonate of potash: vid. *Formation of Cyanogen* (p. 382). 2. The nitrogenous charcoal forms cyanide of potassium directly with the carbonate of potash: vid. *Formation of Cyanogen* (p. 382). Hence uncharred animal matter, which gives off a larger quantity of carbonate of ammonia, likewise yields a greater quantity of cyanide of potassium. [According to Desfosses (p. 383), the quantity of cyanide obtained is the same in both cases, but manufacturers state the contrary.] As ferrocyanide of potassium is decomposed at a red heat, it cannot exist ready formed in the fused product from the the furnace. Hence, if this mass be treated with brandy, that liquid dissolves out all the cyanogen in the form of cyanide of potassium, and the residue, if afterwards treated with boiling water, does not yield even a trace of ferrocyanide of potassium. But if the alcoholic solution be digested with the lixiviated residue and with water, the liquid acquires a yellow colour, because the cyanide of potassium is then converted into ferrocyanide. Hence it appears that this conversion does not take place till the fused mass from the furnace is dissolved in hot water. It is effected, according to the above-mentioned modes of formation of ferrocyanide of potassium, partly by the metallic iron in the fused mass, partly by the sulphide of iron likewise contained therein. The formation of this last-mentioned compound is due to the 12 or 16 per cent. of sulphate of potash usually present in the crude potash, this sulphate being reduced by the charcoal to sulphide of potassium, which then acts both upon the admixed iron filings and upon the iron in the melting vessels

(which are thereby perforated in the course of 10 or 12 fusions), forming an easily fusible sulphide of iron and potassium, which diffuses itself through the whole mass. Since the quantity of iron present is rarely sufficient to convert all the cyanide of potassium into ferrocyanide, and consequently a considerable quantity of cyanide remains in the solution, and is decomposed during the evaporation into ammonia and formiate of potash, the quantity of ferrocyanide obtained, which should amount to 30–35 per cent., does not actually exceed 15 per cent. Metallic iron or sulphide of iron should therefore be added to the aqueous solution of the fused mass; or the solution should be mixed, during the ebullition, with green vitriol, till the black precipitate of sulphide of iron (produced by the sulphide of potassium) begins to be permanent. The mother-liquid decanted from the crystals of ferrocyanide which separate on cooling, then contains sulphate of potash and sulphide of potassium.—Moreover, to 100 parts of crude potash, according to the quantity of sulphate which it contains, there must be added from 12 to 20 parts of iron-filings, in order to convert all the sulphide of potassium formed in the process into sulphide of iron and potassium; otherwise the sulphide of potassium will give up part of its sulphur to the cyanide of potassium, thereby converting it into sulphocyanide, whereby a certain portion of the cyanide will be rendered unavailable for the formation of ferrocyanide. At the same time, a sufficient quantity of sulphide of iron is formed in the mass to convert all the cyanide of potassium into ferrocyanide.—A certain quantity of cyanate of potash may likewise be formed in the fusion, partly from access of air, partly because cyanide of potassium and sulphate of potash form cyanate of potash and sulphide of potassium by double decomposition. [Must not the excess of charcoal present reconvert the cyanate of potash into cyanide of potassium?] This cyanate of potash is afterwards resolved, on dissolving the fused mass in water, into carbonic acid and ammonia. (Liebig, *Ann. Pharm.* 38, 20.)

If the fused mass obtained from 100 lbs. of potash, 400 lbs. of horn-charcoal, and 10 lbs. of iron filings, be pulverized and washed in a funnel with a mixture of equal parts of water and alcohol of 36° Bm. as long as anything is dissolved out, the wash-liquid separates into two layers, the lower containing carbonate of potash, and the upper but a small quantity of cyanide of potassium; the residue thus exhausted gives up to hot water a quantity of ferrocyanide of potassium equal to that which would be obtained in the ordinary way from the unwashed fused mass. Hence it follows that the fused mass—at least that which is prepared on the large scale—contains ferrocyanide of potassium already formed; indeed, if this salt were not formed till the mass was digested in water, the lixiviating pans, which are made of sheet-iron, would soon be corroded, whereas they last for ten years and more. (Runge, *Pogg.* 66, 95.)

Alcohol of 83 p. c. extracts from the fused mass only a small quantity of cyanide of potassium, together with sulphocyanide, and the solution, when evaporated in an open vessel, gives off ammonia and leaves bicarbonate of potash; with sesquichloride of iron it forms a blood-red mixture, which when exposed to sunshine and to the air, assumes a yellow colour, and deposits crystals of ferrocyanide of potassium.—The mass, if digested in water, after exhaustion with alcohol, gives up ferrocyanide of potassium to the water.—If an excess of iron be used in the preparation, the fused mass, when digested with alcohol, imparts no sulphide of potassium to that liquid, for hydrochloric acid added to the solution causes no evolution of sulphuretted hydrogen; but from the

undissolved residue water extracts sulphide of potassium, and the clear aqueous solution, if evaporated even at a low temperature, deposits a large quantity of black mud. [The sulphide of potassium combined with the sulphide of iron resists the solvent action of alcohol, but dissolves in water together with a portion of the sulphide of iron, which is then precipitated in proportion as the sulphide of potassium is decomposed by evaporation in contact with the air.]—The solution obtained from the fused mass in its ordinary state, acquires a brighter yellow colour by continued digestion in an open vessel, not by taking up more ferrocyanide of potassium, but by taking up sulphide of potassium [which is perhaps transformed from monosulphide into polysulphide]. The fused mass, when heated with water in a vessel from which air is excluded, does not give off hydrogen gas. [This is not a necessary consequence, provided a sufficient quantity of sulphide of iron be present.] Even if the air be excluded as far as possible during the fusion, the fused mass on being dissolved in water, gives off a large quantity of ammonia, and still more if green vitriol be added; this salt likewise does injury by converting a portion of the potash into sulphate.—The mother-liquor of the crystals of ferrocyanide of potassium contains large quantities of formiate and bicarbonate of potash. (J. J. Stäger, *Epistolary communication.*)

A fused mass from the works of Otto Pauli at Ettling gave up to boiling alcohol of 34° Bm., a small quantity of sulphocyanide and sulphide of potassium, but no cyanide; for the liquid, on being mixed with a ferroso-ferric salt, and then with hydrochloric acid, yielded no prussian blue; when the alcohol was diluted with water, it dissolved out, on boiling, a large quantity of ferrocyanide of potassium, which crystallized as the liquid cooled. This fused mass gave off no perceptible quantity of ammonia when boiled with water.

¶ Possoz and Boissière (*Compt. rend.* 26, 203) prepare ferrocyanide of potassium by means of the nitrogen of the air, by passing a current of air over charcoal powder saturated with 30 p. c. of carbonate of potash, and heated to whiteness for 10 hours in wide earthen cylinders placed in an upright position. The charcoal, after thorough ignition, is mixed with pulverized native carbonate of iron and lixiviated. (For a description and drawing of the apparatus, vid. *London Journal of Arts*, 1845, 380; also *Repertory of Patent Inventions*, 1847, 280.) ¶

Commercial ferrocyanide of potassium is often contaminated with carbonate and sulphate of potash. It may be purified by dissolving it in the smallest possible quantity of hot water, leaving the sulphate of potash with part of the ferrocyanide of potassium to crystallize by cooling; decanting the mother-liquid and mixing it with alcohol; washing the precipitated ferrocyanide of potassium with alcohol; and crystallizing it once more from water.

Preparation on the small scale.—By adding pure prussian blue to boiling potash-ley as long as its colour is thereby changed to brown; then filtering, washing, and evaporating the solution to the crystallizing point. The salt thus obtained may be contaminated,—especially if the prussian blue be not very pure—with carbonate, phosphate, sulphate and aluminate of potash, with carbonate of ferric oxide and potash (Proust), and with *green prussiate of potash*. It must be purified by picking out the crystals, and repeatedly dissolving and recrystallizing, or, according to Berzelius, by heating the salt first gently till it effloresces, and afterwards to the melting point; dissolving it in water, which leaves

charcoal and carbide of iron undissolved; adding acetic acid to convert the carbonate and hydrocyanate of potash contained in the solution into acetate; precipitating the sulphuric acid present by means of an equivalent quantity of acetate of baryta; filtering, evaporating, precipitating the ferrocyanide of potassium by alcohol; and crystallizing it twice from solution in hot water, after which it exhibits a pale yellow colour; or, according to Klaproth, by adding dilute sulphuric acid to the aqueous solution as long as any precipitate of prussian blue is formed; filtering; evaporating; picking out the crystals of ferrocyanide of potassium; dissolving them in water, and removing the rest of the sulphuric acid by baryta-water; or, according to Henry, by heating the alkaline ley filtered from the decomposed prussian blue with a small quantity of sulphuric acid for an hour; filtering; repeating the treatment with sulphuric acid, if that acid still throws down prussian blue; then precipitating the liquid with sulphate of copper; exhausting the washed precipitate with aqueous solution of potash; filtering; and removing any sulphuric acid that may yet be present by evaporation and cooling (whereupon a small quantity of sulphate of potash crystallizes out), and then by adding a small quantity of baryta-water.

Lastly, the crystallized ferrocyanide of potassium obtained by either of these methods must be freed from water by heating its powder to 100°.

Properties. White powder or friable mass; neutral to vegetable colours, inodorous, and having a sweetish, saline, somewhat bitter taste.

	According to Berzelius.			Robiquet.
6 C	36	19·53	42·91	
3 N	42	22·77		
Fe	28	15·18		14·42
2 K	78·4	42·52		11·36
K^2FeCy^3	184·4	100·00		98·69

Decompositions. Ferrocyanide of potassium fuses at a heat a little below redness, and if the air be excluded, giving off nitrogen gas with slow emission of bubbles, and leaves a mixture of cyanide of potassium mixed with bicarbide of iron (V., 219 f; Berzelius):

$$C^6N^3FeK^2 = 2C^2NK + FeC^3 + N.$$

If but a trace of water be present, it gives off, besides the nitrogen, small quantities of carbonic acid, hydrocyanic acid, and ammonia. (Geiger, *Ann. Pharm.* 1, 59.) The salt still retains water, even after being dried as completely as possible, and therefore at the commencement yields carbonic acid, hydrocyanic acid, ammonia, carbonic oxide, and marsh-gas; the residue contains, in addition to cyanide of potassium, not carbide of iron, but a mixture of iron and charcoal; for the iron is magnetic, rusts under water, and dissolves in dilute acids with evolution of hydrogen. (Robiquet.) Ferrocyanide of potassium ignited with vitrefied boracic acid, which likewise always retains a small quantity of water, also gives off, with strong intumescence, marsh-gas, carbonic oxide, carbonic acid, hydrocyanic acid, and ammonia, but no cyanogen. (Robiquet.)

2. Ferrocyanide of potassium heated nearly to redness in contact with the air and continually stirred, is converted by oxidation into ferric oxide and cyanate of potash; but the moisture in the air causes it likewise to give off a small quantity of ammonia. (Campbell, *Ann. Pharm.* 28, 52.) A mixture of ferrocyanide of potassium and peroxide of manganese set on fire in the air, burns with a glimmering light, forming

cyanate of potash and sesquioxide of iron (Wöhler, Liebig): *vid. Cyanate of Potash.* A finely pulverized mixture of 1 pt. dry or crystallized ferrocyanide of potassium and from $1\frac{1}{2}$ to 2 pts. peroxide of manganese, formed into a cone and set on fire by a live coal, burns with continued glow, giving off a large quantity of carbonate of ammonia, and forming a brown mixture of cyanate of potash, ferric oxide and manganoso-manganic oxide; the interior of the cone is green, and will likewise burn away with a glimmering light if exposed to the air while yet warm. (Liebig, *Kastn. Arch.* 6, 147.) The residue also contains cyanide of potassium (Wöhler, *Pogg.* 5, 386), together with a large quantity of carbonate of potash. (Campbell.)

3. Ferrocyanide of potassium is instantly decomposed by fusion with nitrate of ammonia, ferric oxide being left behind. (Emmett, *Sill. Amer. J.* 18, 258.) When mixed with $\frac{2}{3}$ of its weight of nitre, and introduced by successive portions into a red-hot crucible, it explodes and yields a black mixture of undecomposed ferrocyanide of potassium, cyanate of potash, carbonate of potash, sesquioxide of iron [metallic iron ?], and charcoal.

4. Ferrocyanide of potassium, crystallized or in the state of aqueous solution, decomposes when exposed to light (but not in the dark), giving off hydrocyanic acid, separating ferric oxide or prussian blue, and acquiring an alkaline reaction. (N. Fischer, *Kastn. Arch.* 9, 345.) The solution enclosed in a sealed tube and exposed to the sun, deposits a brown powder, becomes alkaline, and smells of hydrocyanic acid. The yellow solution exposed to air and light, especially to direct sunshine, becomes green; deposits, after some time, a blue powder; acquires an alkaline reaction; and, after being exposed for a considerable time to air and light, no longer yields square tables when crystallized, but dendritic efflorescences. The crystals, when finely pulverized, likewise undergo a similar change in sunshine, the yellow colour changing to greenish blue; this change takes place most quickly in the salt precipitated by alcohol from its aqueous solution. On subsequent solution in water, a blue or sometimes a brown powder then separates. (N. Fischer.) The aqueous solution diluted till it becomes colourless, is quite permanent when kept in the dark, and in a vessel completely filled with it; but on exposure to light, it deposits yellow sesquioxide of iron, the quantity of which increases on boiling the solution; if the bottle is but partially filled, the odour of hydrocyanic acid becomes apparent on opening it after insolation. Linen or paper saturated with the aqueous solution and dried in the shade, gives off no hydrocyanic acid, and exhibits scarcely any colour; but after drying in the sun, during which it evolves hydrocyanic acid, it exhibits a yellow colour; linen which has been thus saturated, and has acquired a strong yellow colour by several days' insolation, afterwards forms in water a deep yellow solution, which on boiling deposits ferric oxide, and acquires an alkaline reaction. (Schönbein, *Pogg.* 67, 87.) The aqueous solution boiled in an open vessel, gives off ammonia (Hollander, Wach); but when boiled in a retort, it evolves hydrocyanic acid. (Wach, *Schw.* 51, 449.)

5. In the voltaic circuit, the aqueous solution of ferrocyanide of potassium yields ferricyanide of potassium at the positive pole, without evolution of gas, whilst hydrogen and potash pass over to the negative pole. If the current be reversed after this decomposition has taken

place, potash appears at the then negative pole,—and at the positive pole, not ferricyanide of potassium, but a substance which does not redden litmus, is quickly converted into prussian blue, and is probably, therefore, protocyanide of iron. (Smee.) Schönbein (*J. pr. Chem.* 30, 145) likewise obtained ferricyanide of potassium at the positive pole.

6. *Chlorine gas* passed through the solution of ferrocyanide of potassium, till that solution no longer forms a blue precipitate with ferric salts, converts it into ferricyanide and chloride of potassium (Gm.):

$$2K^2FeCy^2 + Cl = 3KCy,Fe^2Cy^3 + KCl.$$

If the passage of the chlorine be still continued, the ferricyanide of potassium undergoes a further decomposition which will be explained hereafter (p. 470). *Bromine* also converts ferrocyanide of potassium into ferricyanide. (Smee.) *Iodine* acts upon aqueous ferrocyanide of potassium less powerfully than chlorine and bromine, but appears also to convert part of that compound into ferricyanide. The aqueous solution of 1 At. ferrocyanide of potassium readily dissolves about 1 At. iodine. The dark-red solution, which contains a large quantity of free iodine, forms prussian blue, both with ferrous and with ferric salts. When left to evaporate spontaneously, it gives off iodine and leaves a whitish amorphous mass which contains iodide of potassium, and is either a peculiar compound (*iodoferrocyanate of potash*), or a mixture of iodide of potassium with ferrocyanide or ferricyanide of potassium; this latter view of its composition, however, is inconsistent with the absence of crystallization. The same residue is obtained by evaporating the aqueous solution of ferricyanide of potassium mixed with iodine. If the residue be again dissolved in water and evaporated, a dark substance is deposited, and crystals of ferrocyanide of potassium are again produced. The solution of the residue in water yields the following precipitates with heavy metallic salts: With *bismuth*, a white precipitate changing to yellow; *zinc* and *lead*, white; *copper*, dark brown; *corrosive sublimate*, white, changing to green; *silver*, reddish white. (Smee, *Phil. Mag. J.* 17, 193.) A warm solution of ferrocyanide of potassium absorbs iodine very abundantly, assuming first an olive-green, and then a black-brown colour. The solution saturated with iodine emits vapours which attack the eyes strongly, and on cooling deposits a brown-red saline magma. If only so much iodine be added as to give the solution an olive-green colour, and the liquid be then concentrated to a certain point, it yields on cooling a crystalline powder, which after being pressed between paper, forms a golden-yellow, silky mass, which is probably a compound of ferrocyanide of potassium with iodine. When heated, it turns brown, gives off iodine-vapour, and leaves ferrocyanide of potassium. Its aqueous solution exhibits with ferrous and ferric salts the same reactions as ferrocyanide of potassium, and gives a red precipitate [mercuric iodide] with mercuric salts. (Preuss. *Ann. Pharm.* 29, 323.) According to Gerdy (*Compt. rend.* 16, 25; also *J. pr. Chem.* 29, 181), iodine does not decompose ferrocyanide of potassium.

7. Ferrocyanide of potassium, either anhydrous or crystallized, when mixed with *sulphur*, and heated somewhat above the melting point of the latter, is converted into a mixture of 2 At. sulphocyanide of potassium and 1 At. sulphocyanide of iron (Berzelius):

$$2KCy,FeCy + 3S = 2KCyS^2 + FeCyS^2.$$

If the heat applied be not sufficient to produce complete decomposition,

protocyanide of iron, which turns blue in the air, remains undissolved when the fused product is digested in water; if, on the contrary, the heat be too strong, the sulphocyanide of iron produced at first is resolved into nitrogen gas, vapour of sulphide of carbon, and a residue of protosulphide of iron. (Berzelius.) In this decomposition, therefore, there are three stages to be distinguished: 1. If the heat applied is but just sufficient to fuse the mixture, the water extracts only the sulphocyanide of potassium, and leaves all the iron in the form of ferrous cyanide.—2. By continued fusion, the latter compound is converted into sulphocyanide of iron.—3. If the fusion be still further continued, the sulphocyanide of iron is decomposed, with emission of blue flames of sulphide of carbon, into sulphide of carbon, mellon, and protosulphide of iron:

$$4C^2NFeS^2 = 2CS^2 + C^6N^4 + 4FeS \text{ (or perhaps also } = 2CS^2 + C^6N^4Fe + Fe^3S^4).$$

The mellon withdraws the potassium from a portion of the admixed sulphocyanide of potassium, to form mellonide of potassium; the sulphocyanogen thus set free is reconverted into mellon, which decomposes a fresh quantity of sulphocyanide of potassium, &c., &c., and thus, if the heat be continued for a considerable time, a product may be obtained, consisting chiefly of mellonide of potassium. If a quantity of carbonate of potash, equal to $\frac{1}{10}$ of the ferrocyanide of potassium used, be added to the mass, as soon as the blue flames cease to show themselves, the mass becomes more fluid, and very rich in mellonide of potassium. (Liebig, *Ann. Pharm.* 50, 345.)

8. *Ozone* produced by the slow combustion of phosphorus, converts ferrocyanide of potassium into ferricyanide. Phosphorus completely immersed in aqueous solution of ferrocyanide of potassium, exerts no action upon it; but if the liquid be contained in a narrow-necked vessel, and part of the phosphorus project out, the liquid acquires an acid reaction from formation of phosphoric acid, and becomes reddish yellow, in consequence of the production of ferricyanide of potassium, so that after neutralization, it forms prussian blue, no longer with ferric but with ferrous salts. This decomposition takes place very slowly at 9°, but quickly above 15°. (Smee.) The transformation is due to Schönbein's ozone. If crystals of ferrocyanide of potassium be suspended within a carboy—such as those used for containing oil of vitriol—at the bottom of which a piece of phosphorus is slowly burning, the crystals soon acquire a crimson colour on the surface, and after 36 hours, are found to be covered with a red crust a line in thickness, and consisting of a loose aggregate of small crystals, the solution of which no longer gives a blue colour with ferric salts. On placing pieces of phosphorus an inch long, and clean on the surface, in carboys, covering them half up with water, and exposing them for 12 hours to slow combustion at a temperature of 20°, so that the air in the vessel may become charged with ozone; then shaking the phosphorus and the water out of the vessel; washing it with water to remove phosphorous acid; then pouring in ferrocyanide of potassium, and agitating it with the ozonized air, till the liquid no longer forms a blue precipitate with ferric salts,—the solution acquires a strong alkaline reaction; imparts a blue colour to starch mixed with iodide of potassium, on the addition of sulphuric acid; and yields on evaporation beautiful crystals of ferricyanide of potassium. Two carboys suffice for the complete conversion of 5 grammes of ferrocyanide of potassium. (Schönbein, *Pogg.* 67, 83 and 86.) If ozone be regarded as a higher oxide

of hydrogen, we may suppose that it gives up oxygen to one-fourth of the potassium in the ferrocyanide, thereby forming potash. The blue colouring of starch-paste mixed with iodide of potassium is attributed by Schönbein to the conversion of this potash into peroxide of potassium; it may, however, be due to an excess of ozone taken up by the liquid.

9. Aqueous *iodic acid* converts ferrocyanide of potassium into ferricyanide of potassium, iodate of potash, and iodine. (Smee.) Probably thus:

$$10K^2FeCy^3 + 6IO^5 = 5K^3Fe^2Cy^6 + 5(KO,IO^5) + I.$$

Chloric acid acts in a similar manner, but not so strongly; hence it is necessary to apply heat, which causes an evolution of chlorine.—A mixture of chlorate of potash and dilute hydrochloric acid likewise produces ferricyanide of potassium.—*Chromic acid* does not produce ferricyanide of potassium, but forms prussian blue like other acids.

10. Ferrocyanide of potassium somewhat strongly heated with twice its weight of *nitric acid*, first gives off cyanogen gas, then nitrogen, nitric oxide and carbonic acid, and leaves a mixture of nitrate of potash and ferric oxide. (Thomson.)—Ferrocyanide of potassium forms with nitric acid a coffee-coloured liquid, which when neutralized with potash and filtered, appears greyish yellow, and yields with ferric salts a precipitate of a tolerably dark blue colour. (Döbereiner, *Schw.* 26, 305.)—When ferrocyanide of potassium is heated with moderately strong nitric acid (or aqua-regia), small quantities of cyanogen and carbonic acid are evolved, and a dark-brown liquid is obtained, which, after standing for some time, deposits crystals of nitre, together with prussian blue previously suspended. The brown liquid decanted from this deposit may be kept unaltered for several years, and if left in an open vessel, slowly dries up to a dark-brown extract mixed with nitre. Continued boiling with strong nitric acid does not decompose it. But its mixture with alcohol gradually deposits prussian blue.—When supersaturated with potash or ammonia, it deposits hydrated protoxide of iron, and acquires a light-brown colour, which on the addition of a small quantity of sulphuretted hydrogen water, changes to a splendid *purple*, and on the addition of a larger quantity, to *dark blue;* ultimately, the liquid assumes a green tint, but this proceeds from the flakes of hydrated ferric oxide floating about in it. Sulphurous acid added to the liquid supersaturated with potash, likewise produces a red colour, which however inclines to yellow and never changes to blue.—Protochloride of tin does not produce any red colouring in the liquid.—If the liquid, after supersaturation with potash, be set aside for a day till it ceases to deposit hydrated ferric oxide, a pale, yellowish brown, liquid, alkaline filtrate is obtained, which remains clear and exhibits still finer purple and blue tints with sulphuretted hydrogen; but no green colour is produced, because there are no flakes of ferric hydrate floating in the liquid. The red or blue mixture, which is clear at first, gradually becomes cloudy, even when the air is completely excluded, and in a few hours loses its colour, and deposits a soft white powder (milk of sulphur). On the application of heat, the liquid immediately becomes decolorized, and is converted into a turbid, greenish white mixture.—The alkaline filtrate, on evaporation and ignition, leaves a larger quantity of ferric oxide. (Gm., according to *Handb.* Aufl. 3, 1, 167, and later experiments.)—This brown liquid may perhaps contain a nitro-compound.—Hydrocyanic acid or prussian blue heated with nitric acid does not form a brown liquid.

—Similar effects have been observed by Campbell and Smee: Ferrocyanide of potassium gently heated with strong nitric acid gives off nothing but cyanogen gas, neither hydrocyanic acid, nor nitrous vapours, and yields a black mass, perfectly soluble in water. The liquid reddened by addition of potash and sulphuretted hydrogen (*vid. sup.*), deposits a blue substance, which afterwards turns white, and cannot be prussian blue, since it is formed in an alkaline liquid. Perhaps the red colouring is connected with that which Gregory obtained by dissolving sulphide of nitrogen in alcoholic potash (II., 414). (Campbell, *Ann. Pharm.* 28, 57.) —When ferrocyanide of potassium is dissolved in excess of nitric acid, nitric oxide is evolved; the dark-coloured solution neutralized with potash no longer precipitates ferric salts, but forms a blue precipitate with ferrous salts; when evaporated it yields crystals of nitre, mixed with a small quantity of ferricyanide of potassium. On evaporating with a larger quantity of nitric acid, a black mass is obtained, which tastes sweet at first, but leaves an unpleasant metallic taste in the mouth. (Smee, *Phil. Mag. J.* 17, 194.)—¶ According to Playfair (*Phil. Trans.* 1849, II. 477; *Jahresber.* 1849, 292), the action of nitric acid on ferrocyanides produces a new class of compounds which he calls *Nitroprussides*, and to which he assigns the general formula $Fe^4Cy^{12}N^2O^2,5M$. — When ferrocyanide of potassium is heated with dilute nitric acid, a copious evolution of nitric oxide takes place at first; this, however, soon ceases entirely if the mixture be cooled. Other volatile products are then evolved, viz., cyanogen, hydrocyanic acid, nitrogen, carbonic acid, and apparently also of cyanic acid. The dark-red solution, as it cools, first deposits nitre, and afterwards,—provided too much nitric acid has not been used,— oxamide. The remaining solution contains ferricyanide of potassium, nitroprusside of potassium, and nitre.—[For further details, vid. *Nitroprussides*.] ¶

11. *Chromic acid*, and likewise bichromate and monochromate of potash, transform dissolved ferrocyanide of potassium into ferricyanide; on heating the mixture, a greenish substance is deposited. (Schönbein, *J. pr. Chem.* 20, 145.)

12. Ferrocyanide of potassium strongly heated with 9 pts. of *oil of vitriol* is resolved almost wholly into carbonic oxide, sulphate of potash, sulphate of ammonia, and ferrous sulphate, which on the application of a stronger heat is converted, with evolution of sulphurous acid, into ferric sulphate, and then forms an iron-alum with each of the alkaline sulphates. (Fownes.)—When oil of vitriol is poured upon ferrocyanide of potassium, the mass becomes hot, and gives off a small quantity of hydrocyanic acid. On applying heat, the white pasty mass at first formed dissolves and gives off abundance of carbonic oxide gas, which is pure, excepting that it has a slight garlic odour; no hydrocyanic acid passes over with the gas, but only a trace of formic acid; finally, also, a small quantity of sulphurous acid is evolved. If the heat be continued after all the carbonic oxide has passed over, the ferrous sulphate is converted into ferric sulphate, with copious evolution of sulphurous acid; and the hot liquid deposits white, pearly, micaceous, crystalline laminæ of anhydrous ferrico-ammonio-potassic sulphate, which increase in quantity as the heat is continued.—The first decomposition takes place in the manner represented by the following equation :

$$C^6N^3FeK^3 + 9HO = 6CO + 3NH^3 + 2KO + FeO.$$

The alum-crystals afterwards formed have the composition: $(NH^4O,SO^3$

$+KO,SO^3)+(Fe^2O^3,3SO^3)$. (Fownes, *Phil. Mag. J.* 24, 21; also *Ann. Pharm.* 48, 38.) Döbereiner (*Schw.* 28, 107) had previously obtained pure carbonic oxide gas, and a white residue consisting of sulphate of ammonia, sulphate of potash, and cyanide of iron.—Thomson obtained sulphurous acid and a peculiar combustible gas, 3 volumes of which contained 3 vol. carbonic oxide and 1 vol. hydrogen (*comp.* Berzelius, *Schw.* 30, 57).—Merk (*Repert.* 68, 190), by rapidly distilling ferrocyanide of potassium with oil of vitriol, obtained a distillate containing small quantities of hydrocyanic and hydrosulphocyanic acid, together with formic acid and a sublimate consisting of sulphite of ammonia crystallized in needles.

13. *The stronger acids, added in the state of dilute solution*, and not in too great excess, to a solution of ferrocyanide of potassium, produce no apparent alteration; but subsequent treatment with ether shows that ferroprussic acid has been separated (p. 429). The mixture becomes turbid when heated, boils below 100°, gives off half the cyanogen of the ferrocyanide, in the form of hydrocyanic acid, deposits the white or yellow powder of KFe^2Cy^3, and then contains in solution a compound of the acting acid with three-fourths of the potash which the potassium present is capable of yielding.—Supposing that the ferrocyanide of potassium is not completely decomposed in the cold—which, though not certain, may be assumed as true, when only 3 At. sulphuric acid are used—the equation will be:

$$2K^2FeCy^3 + 3(HO,SO^3) = 3HCy + KFe^2Cy^3 + 3(KO,SO^3).$$

But, if the ferrocyanide of potassium is completely decomposed at the commencement, without the aid of heat, into ferroprussic acid and potash-salt, we must suppose that the ferroprussic acid, when resolved by heat into hydrocyanic acid and KF^3Cy^3, again takes up 1 At. potash from the potash-salt produced:

$$2H^2FeCy^3 + 4(KO,SO^3) = 3HCy + KFe^2Cy^3 + HO + 3KO + 4SO^3.$$

According to calculation, 211·4 parts (1 At.) of crystallized ferrocyanide of potassium, yield 40·5 pts. ($1\frac{1}{2}$ At.) or 19 p. c. of hydrocyanic acid.

100 parts of crystallized ferrocyanide of potassium distilled with 12 pts. ($2\frac{1}{2}$ At.) of oil of vitriol and 20 pts. of water, till 16 pts. have passed over, yield a distillate containing 17·58 pts. of anhydrous prussic acid (=211·4+37·62); the sulphuric acid also constantly produces a small quantity of formic acid. The yellowish white, inodorous, pasty residue, treated with water, gives up a trace of ferrous sulphate [and probably also of sulphate of ammonia] together with the acid sulphate of potash. The insoluble residue, which assumes a light blue colour during washing, exhibits the characters mentioned by Wackenroder (p. 475).—When ferrocyanide of potassium is distilled with aqueous phosphoric acid, a large portion always remains undecomposed; but the phosphoric acid does not give rise to the production of formic acid. According to the *Pharmac. Boruss.*, 100 parts ferrocyanide of potassium distilled with 200 pts. phosphoric acid of sp. gr. 1·13, and 300 pts. alcohol, till a moist, pasty residue remains, yield only 11·49 pts. of anhydrous prussic acid (=211·4 : 24·29). (Wackenroder, *N. Br. Arch.* 2, 33.)

A cold mixture of aqueous ferrocyanide of potassium and dilute sulphuric acid, begins to assume a turbid appearance at 40°, and to deposit a green powder at 60°, but does not give off hydrocyanic acid till heated

to 104 [?]; moreover, part of the hydrocyanic acid is decomposed by the sulphuric acid. Ammonia is found in the residue and a trace also in the distillate; but no formic acid can be detected, perhaps because it is further resolved into carbonic oxide and water.—211·4 pts. of crystallized ferrocyanide of potassium distilled with 108 to 115 pts. of sulphuric acid of specific gravity 1·82 and the requisite quantity of water, yield 40 pts. of anhydrous prussic acid. The more quickly the distillation is conducted, the greater is the quantity of prussic acid obtained, the product varying from 33·9 to 401 pts.; the variation probably depends on the quantity of ammonia formed. When the residue is washed with water, neither iron nor cyanogen is dissolved out. Whichever proportion of sulphuric acid may have been used, the washed green sediment from 211·4 pts. of ferrocyanide amounts, after drying at 100°, to 74·6... 75·23 pts. (35·3.... 35·5 per cent.); it must therefore be regarded as hydrated cyanide of iron together with a very small quantity of cyanide of potassium. [According to page 474, this sediment = KFe^2Cy^3, and should amount to 86·6 pts. from 211·4 pts. of ferrocyanide of potassium.]—211·4 pts. of ferrocyanide of potassium require at least 76·4 pts. ($1\frac{1}{2}$ At.) sulphuric acid of sp. gr. 1·82; but if no more than that quantity be used, the distillation must be continued to dryness, to decompose all the ferrocyanide. If 5 At. sulphuric be used together with water, all the hydrocyanic passes over while the residue is still quite liquid, and 211·4 pts. of ferrocyanide yield from 38 to 40·4 pts. of anhydrous prussic acid, contaminated however with sulphuric acid. But if such a mixture be distilled to dryness at a temperature ultimately rising to 140°, a small additional quantity of hydrocyanic acid passes over [probably because the concentrated sulphuric acid exerts a decomposing action on the KFe^2Cy^3], together with cyanogen and formic or sulphurous acid, so that the total quantity obtained amounts to 42·32 pts. The residue is now porous and blue, and after washing leaves 76·4 pts. of *dark-blue* sediment. The transparent and colourless acid wash-water assumes when exposed to light, first a yellow, then a blue colour, yields a small blue precipitate, and is afterwards found to be free from iron. (Thaulow, *J. pr. Chem.* 31, 234.)

When a concentrated aqueous mixture of ferrocyanide of potassium and sulphomethylate of potash is evaporated and cooled, yellow square tables are obtained; and the highly alkaline mother-liquid, on being further evaporated and cooled, yields colourless tables. The former contain 29·73 per cent. of potassium, 15·39 Fe, and 13·5 water; hence their formula is $4KCy,3FeCy,C^2H^3O,C^2N + 8Aq$. [According to Gregory's own description, they appear to be nothing but impure ferrocyanide of potassium.] The colourless tables, after drying at a gentle heat, are anhydrous; when strongly heated, they fuse, give off first a vapour having an ethereal odour, and afterwards vapours which smell of garlic—swell up, and leave a residue of fused bisulphate of potash. They contain 34·71 per cent. of potash, 35·12 sulphuric acid, 7·19 carbon acid, and 1·67 hydrogen; no iron. [The nitrogen was not determined.] Their composition is therefore: $3(KO,2SO^3) + C^2H^3O + C^2H^3Cy$. Hence 3 At. ferrocyanide of potassium and 3 At. sulphomethylate of potash yield 1 At. of the yellow salt, 1 At. of the colourless salt, and 2 At. free potash. (Gregory, *Ann. Pharm.* 22, 269.) [Deserves further investigation.]

14. A mixture of 1 pt. ferrocyanide of potassium, either dry or crystallized, with 1 pt. *peroxide of manganese* and 2 pts. *bisulphate of potash*, gives off, when heated, carbonic oxide, carbonic acid, and a small

quantity of nitrogen, together with hydrocyanic acid, hydrocyanate of ammonia, and carbonate of ammonia, and leaves a residue whose aqueous solution exhibits an alkaline reaction, and gives off sulphuretted hydrogen when treated with acids. (Harzen-Müller, *Ann. Pharm.* 58, 102.) According to Döbereiner (*Gilb.* 74, 421), 1 At. ferrocyanide of potassium heated with 3 At. peroxide of manganese and 6 At. oil of vitriol, gives off cyanic acid.

15. Aqueous ferrocyanide of potassium digested for a considerable time with finely pulverized *peroxide of manganese*, yields very pure ferricyanide of potassium. The addition of sulphuric acid accelerates the decomposition, but the product is then contaminated with sulphate of potash. (Smee.) Finely pulverized *peroxide of lead* acts more quickly than peroxide of manganese. As the formation of ferricyanide of potassium goes on, the liquid becomes continually deeper in colour; after two hours' boiling, the decomposition is complete. The peroxide is at the same time converted into a white mixture of hydrate and carbonate of lead. The yellow liquid, when evaporated, yields crystals of ferricyanide of potassium, and a mother-liquor containing carbonate of potash. The carbonic acid is probably derived from the air:

$$2K^2FeCy^3 + PbO^2 = 3KCy,Fe^2Cy^3 + KO + PbO.$$

Red lead, on the contrary, exerts no action on ferrocyanide of potassium, either when placed in contact with it for a week, or when boiled with it. (Schönbein, *J. pr. Chem.* 30, 146.)

16. *Mercuric oxide* boiled with aqueous solution of ferrocyanide of potassium gradually throws down the iron in the form of reddish yellow ferric oxide, which however contains a certain portion of cyanogen, so that, on dissolving it in hydrochloric acid, prussian blue is left behind; the liquid contains cyanide of mercury, and when evaporated, leaves also carbonate of potash. (Vauquelin, *Schw.* 25, 74.) Perhaps in this manner:

$$K^2FeCy^3 + 3HgO = 3HgCy + 2KO + FeO.$$

The FeO is then converted into Fe^2O^3 by taking up O from another portion of HgO, and the potash into carbonate by the carbonic acid of the air; for Duflos (*Schw.* 65, 114), by boiling the analogous compound, ferrocyanide of barium, with mercuric oxide, obtained a solution of cyanide of mercury and caustic baryta, and a precipitate containing ferric oxide together with mercurous oxide and metallic mercury.—By sufficiently long boiling the iron may be completely separated. (Berzelius.) The ferric oxide precipitated by the mercuric oxide dissolves in hydrochloric acid, with evolution of hydrocyanic acid; and the solution evaporated after precipitation by ammonia, yields a small quantity of chloride of potassium. The ferric oxide appears then to retain cyanide of potassium. (Gm.)—If the quantity of mercuric oxide added to the boiling solution is not sufficient to decompose the ferrocyanide completely, the liquid, on cooling, deposits pale yellow rhombic tables [a compound of ferrocyanide of potassium with cyanide of mercury?]. (Preuss, *Ann. Pharm.* 29, 324.)—When 1 pt. ferrocyanide of potassium is boiled with 2 pts. *monosulphate of mercuric oxide* and 8 pts. of water, a small whitish precipitate separates, and a solution is formed containing cyanide of mercury and sulphate of potash (Desfosses, *J. Chim. méd.* 6, 261); according to Duflos, this solution also contains ferric oxide.—To decompose the ferrocyanide of potassium

completely, 7 At. (=7 . 148) mercuric sulphate are required for every 2 At. (=2 . 211·4) of the ferrocyanide. When these proportions are used, the precipitate consists of reduced mercury, with only a small quantity of greenish white powder. (Duflos, *Schw.* 65, 112.) The equation is therefore:

$$2K^2FeCy^3 + 7(HgO,SO^3) = 6HgCy + 4(KO,SO^3) + Fe^2O^3,3SO^3 + Hg.$$

When ferrocyanide of potassium is boiled with *nitrate of mercury* [mercuric nitrate?], the compound KCy,HgCy,2Aq. crystallizes out in white micaceous laminæ. Similar laminæ = KCy,HgCy,Aq. are obtained by boiling the ferrocyanide with corrosive sublimate. (Desfosses.) [In these reactions, the quantity of mercury was probably insufficient for complete decomposition.] The hot solution of ferrocyanide takes up a large quantity of *mercuric iodide*, and on cooling deposits a compound of iodide of potassium and mercuric cyanide crystallized in laminæ. (Preuss.)

17. When solution of ferrocyanide of potassium is boiled with a few drops of *sesquichloride of iron*, a certain quantity of ferricyanide of potassium is formed, so that the liquid yields a deep blue precipitate with ferrous salts (Williamson, *Ann. Pharm.* 57, 238):

$$3K^2FeCy^3 + Fe^2Cl^3 = K^3Fe^2Cy^6 + 3FeCy + 3KCl.$$

A small quantity of ferricyanide of potassium is also formed on boiling a solution of the ferrocyanide with a large excess of prussian blue.

18. When ferrocyanide of potassium is heated with sal-ammoniac, either in the wet or in the dry way, hydrocyanate of ammonia is volatilized, while chloride of potassium and chloride of iron remain. (Duflos, *Schw.* 65, 106; Bineau, *Ann. Chim. Phys.* 67, 231.)

19. The aqueous solution of ferrocyanide of potassium forms precipitates with most salts of the earthy alkalis, earths, and heavy metallic oxides, the potassium being oxidized by the oxygen in the base of the salt, and remaining dissolved in combination with the acid, whilst the precipitate consists of ferrocyanide of potassium, in which the potassium is replaced by the metal of the base; *e. g.*:

$$K^2FeCy^3 + 2(PbO,NO^5) = Pb^2FeCy^3 + 2(KO,NO^5).$$

Frequently, however, the newly-formed cyanogen-compound carries ferrocyanide of potassium down with it, especially if to 1 At. ferrocyanide of potassium there be added only 1 At. instead of 2 At. of the other salt; in this case, the precipitate generally contains 1 At. ferrocyanide of potassium with 1 At. of the newly formed ferrocyanide. (Mosander, *Pogg.* 25, 390.) But even when the salt of the earthy or heavy metal is added in very large excess to the ferrocyanide of potassium, the precipitate generally contains small quantities of the latter salt, which are difficult to remove, even by long-continued digestion with the supernatant liquid.—As, in precipitating ferrocyanide of potassium with the salt of a heavy metal, the excess of acid in the latter might [after a while] separate cyanide of iron, and thereby, in very dilute solutions, render the reaction uncertain, it is best to mix the solution of 11 pts. ferrocyanide of potassium in 100 pts. water with ½ vol. aqueous ammonia, add this solution to the heavy metallic salt in such proportion that the liquid may still smell of ammonia, and then add acetic acid in slight excess, whereupon the precipitate will immediately appear. An acid solution containing only

$\frac{1}{300,000}$ pt. of copper yields, when thus treated, an immediate precipitate, and a solution containing only $\frac{1}{500,000}$ exhibits a red tint in 18 hours; whereas by the ordinary process only $\frac{1}{130,000}$ pt. of copper can be detected in a liquid. (Levol, *N. J. Pharm.* 3, 211; also *J. pr. Chem.* 30, 361.) ¶ In some cases also, as in that of copper, the ammoniacal solution of the ferrocyanide may be left to evaporate on a small white porcelain dish; the ammonia then escapes, and the ferrocyanide of copper is left with its characteristic colour: extremely small quantities of copper may be thus detected. (Warington, *Chem. Soc. Qu. J.* 5, 137.) ¶

Combinations. With Water. *Crystallized Ferrocyanide of Potassium.* In crystallizing from its aqueous solution, ferrocyanide of potassium takes up 3 At. water, and yields crystals belonging to the square prismatic system; they are lemon-yellow by reflected, and pale yellow, by transmitted light. *Fig.* 26 and other forms; cleavage easy parallel to *p*, less easy parallel to *e*; $e : e'' = 137°$; $p : e = 111° 30'$; $p : a = 119° 9'$. (Brooke, *Ann. Phil.* 22, 41.) *Fig.* 25; $e : e'' = 136° 22'$; $p : e = 111° 52'$; $p : a = 119° 40'$; $e : a = 138° 55'$. (Bunsen, *Pogg.* 36, 404.)—Sp. gr. 1·833 (Thomson); soft and somewhat flexible.—The crystals are permanent in the air; at 60° they begin to give off their water, which however escapes but slowly even at 100°, unless the fine powder be continually stirred in contact with the air.—Oil of vitriol turns the crystals white by abstracting their water. (Thomson.)—The crystals contain exactly so much HO, that they may be regarded as anhydrous hydrocyanate of ferrous oxide and potash, $2(KO,HCy)+FeO,HCy$.

			Berzelius.	Ure.	Ittner.	Döbereiner.	R. Phillips.
6 C	36·0	17·03					
3 N	42·6	19·87					
Fe	28·0	13·24	12·94	14·00			13·58
2 K	78·4	37·09	37·06				36·75
3 HO	27·0	12·77	12·70	12·88	12	12	12·50
$C^6N^3FeK^2+3Aq$	211·4	100·00					

R. Phillips (*Phil. Mag. Ann.* 1, 110; also *Kastn. Arch.* 11, 239).—Proust found 10, and Porrett, Thomson, and Robiquet 13 per cent. of water of crystallization.

			Berzelius.	Ure.	Döbereiner.	Porrett.	Ittner.
2 KO	94·4	44·66	44·62	44 8	42·20	41·68	39
FeO	36·0	17·03	16·64	18·0	20·68	16·33	
3 HCy	81·0	38·31			36·31	36·76	
$2(KO,HCy),FeO,HCy$	211·4	100·00			99·19	94·77	

Ferrocyanide of potassium dissolves readily in water, forming a pale yellow solution; it dissolves more abundantly in hot than in cold water, and is precipitated from the solution by alcohol, in which it is quite insoluble, in yellowish white, pearly scales.—Specific gravity of the solution saturated at 8°=1·130. (Anthon.)—The solution absorbs cyanogen gas abundantly (acquiring, according to Smee, a dark colour), but without formation of ferricyanide of potassium. (Gm. *Schw.* 34, 339; Smee.)

Ferrocyanide of potassium dissolves in excess of oil of vitriol, with rise of temperature, but without effervescence, and forms a colourless liquid, which, on exposure to damp air, deposits small needles. These

crystals contain several atoms of sulphuric acid to 1 At. ferrocyanide of potassium; they dissolve in water, forming a solution which contains ferroprussic acid and acid sulphate of potash; alcohol of sp. gr. 0·81 extracts ferroprussic acid from them, and leaves sulphate of potash. (Berzelius.)

Green Ferrocyanide of Potassium.—When ferrocyanide of potassium is prepared by treating impure commercial prussian blue with caustic potash-ley (p. 456), there sometimes remains, after the yellow ferrocyanide has crystallized out, a brown, thickish, efflorescent mother-liquor. On neutralizing this liquid with acetic acid, and adding alcohol (which takes up the acetate of potash formed from the carbonate in the mother-liquor), a green mass separates out. This substance forms with water a dark green solution, from which the salt crystallizes by cooling or evaporation in greenish grey scales, containing the same quantities of potassium and iron as the yellow salt. The aqueous solution of these crystals turns brown in the air. If this salt be again dissolved in water, and the solution evaporated at a gentle heat, a green powder is deposited, and the salt is thereby rendered more crystallizable. On heating the dehydrated green salt in a covered crucible, till it no longer gives off vapours which smell of ammonia, and dissolving the residue in water, there remains a quantity of carburetted iron larger than that which would be obtained by heating the yellow salt to the same degree; and the solution then contains yellow ferrocyanide of potassium, together with small quantities of cyanide of potassium and carbonate of potash. (Berzelius, *Schw.* 30, 64.)

Ferricyanide of Potassium. $3KCy,Fe^2Cy^3=C^6N^3K^3,C^6N^3Fe^2$.

Ferridcyanide of Potassium, Ferrosesquicyanide of Potassium, Red Ferrocyanide of Potassium, Red Ferroprussiate of Potash, Red Prussiate of Potash; rothes Cyaneisenkalium, rothes Blutlaugensalz, Kaliumeisencyanid, Ferridcyankalium. In the state of aqueous solution, it may also be regarded as *Hydrocyanate of Ferric-oxide and Potash.*

Formed from ferrocyanide of potassium, when the latter is deprived of ¼ of its potassium by oxygen, chlorine, bromine, &c.

Preparation. 1. Chlorine gas freed from hydrochloric acid by washing with water, is passed with constant agitation through a cold aqueous solution of ferrocyanide of potassium, till a sample taken out of the liquid, (the yellow colour of which becomes continually deeper,) on being added to the solution of a ferric salt perfectly free from ferrous salt, no longer throws down prussian blue, but forms a clear brown mixture. The liquid is then evaporated over the water-bath till crystals begin to form. The crystals increase in quantity as the water-bath cools, and may be purified by repeated crystallization. (Gm. *Schw.* 34, 325.)—If the chlorine acts unequally on the different parts of the liquid, or in excess, a further decomposition takes place, resulting in the formation of chloride of cyanogen, and a dark red liquid is produced, which, on evaporation, deposits prussian green (p. 446), whereby the purification of the salt is rendered much more difficult. Hence it is necessary to stir the liquid constantly, and test it frequently with a ferric salt. The crystals obtained by the first evaporation are often mere needles; but on separating them from the mother-liquor, washing them with cold water, dis-

solving in hot water, again evaporating, and repeating this process several times, the liquid ultimately purified by filtration yields thick crystals, an inch in length. The mother-liquor is mixed with the wash-water, and again evaporated as long as red crystals continue to form. The process to be followed is more particularly described in Vol. I. p. 15, under the head of *Methodical Purification by Crystallization*. The mother-liquid, after this treatment, contains scarcely anything but chloride of potassium, and sometimes a small quantity of reproduced ferrocyanide; hence the crystals last separated from the mother-liquid must be tested with a ferric salt, to see whether they contain ferrocyanide of potassium, and in that case they must be again treated with chlorine. The chloride of potassium contained in the unpurified solution appears to be the cause of its effloresceing so rapidly during evaporation and cooling; for this reason it is advisable to use vessels with deep sides. Lastly, it is to be observed, that larger crystals are produced by hot evaporation than by cooling in rapidly boiled solutions. (Gm.)

To remove the prussian green produced by excess of chlorine, which is apt to pass through the filter, and interferes with the purification of the crystals, Posselt (*Ann. Pharm.* 42, 170), after treating the solution with chlorine, and boiling it down to the crystallizing point, adds to it a few drops of potash, sufficient to destroy the green precipitate, then filters to remove the ferric oxide, and leaves the solution to crystallize by slow cooling. An excess of potash must be avoided, otherwise ferrocyanide of potassium will be formed. A certain quantity of ferrocyanide is, however, produced in the decomposition of the prussian green (p. 447).

¶ Rieckher (*Jahrb. pr Pharm.* 15, 1) passes chlorine gas slowly through a cold dilute solution of the yellow prussiate, till the liquid exhibits a dark red colour by transmitted light; then evaporates quickly to dryness; treats the residue with four times its weight of water; and boils the filtrate down to half its bulk.—Kolbe (*Jahrb. pr. Pharm.* 16, 322) adds chlorate of potash and hydrochloric acid in small portions to a boiling solution of the yellow prussiate. ¶

2. By placing a solution of ferrocyanide of potassium in the circuit of the voltaic battery (p. 458), or by digesting it with finely pounded manganese (p. 465), Smee (*Phil. Mag. J.* 17, 193) obtained very pure ferricyanide of potassium.

3. Small quantities may be formed by the action of ozone. (Schönbein, p. 460.)

4. Prussian blue is decomposed at a gentle heat by chloride of potash (III., 57), and the filtrate evaporated to the crystallizing point. (Kramer, *J. Pharm.* 15, 98.)—The product thus obtained is mixed with a much larger quantity of foreign potash-salts than that produced by (1), and is, therefore, more difficult to purify.

5. An aqueous solution of ferrocyanide of potassium is digested with an excess of the blue substance $K^2Fe^8Cy^{12}$ (p. 477), which completely converts it into ferricyanide, and the resulting solution filtered and evaporated. The residue on the filter, which has become paler in colour by taking up $\frac{1}{4}$ of the potassium contained in the ferrocyanide, may be again deprived of this quantity of potassium by digestion with nitric acid, so that it may be repeatedly used for converting fresh quantities of the yellow salt into the red. (Williamson, *Ann. Pharm.* 57, 231.)

8. Aqueous cyanide of barium is precipitated by a mixture of ferric sulphate and sulphate of potash. (F. & E. Rodgers.) [Does not succeed

well.] (On the preparation of this salt, see also Winkler, *Mag. Pharm.* 19, 262; Robiquet & Clemson, *J. Pharm.* 14, 356; also *N. Tr.* 17, 2, 155.)

Aurora-coloured, transparent, highly lustrous prisms, belonging to the right prismatic system. *Fig.* 66, but without the *t*- and *y*- faces, and without the two faces below *aa*; *m*-face often very broad; cleavage parallel to *m*; $u : u = 100°$; $a : u = 137°$ nearly.—Forms an orange-yellow powder, and has a slightly astringent saline taste. Perfectly neutral. (Gm.) Tastes slightly soapy. Turns violets slightly green. (Girardin.) [Because yellow and blue together make green.]

	Crystallized.			Gm.
12 C	72·0	....	21·84 }	49·00
6 N	84·0	....	25·49 }	
2 Fe	56·0	....	16·99	17·22
3 K	117·6	....	35·68	35·65
$3KCy,Fe^2Cy^3$	329·6	....	100·00	101·87

1. The crystals, when heated in close vessels, decrepitate loudly, crumble to a brown powder, give off cyanogen, mixed with a small quantity of nitrogen, and leave a greyish black porous residue, from which water extracts cyanide and ferrocyanide of potassium, and a brown substance resembling paracyanogen, leaving a residue of carbide of iron mixed with a small quantity of prussian blue. (Gm.) Boudault (*N. J. Pharm.* 7, 437; also *J. pr. Chem.* 36, 23) obtained cyanogen, nitrogen, cyanide of potassium, ferrocyanide of potassium, and carbide of iron[?].— 2. In the flame of a candle, the crystals burn with decrepitation and sparkling. When ignited in contact with the air, they give off more cyanogen than when ignited in a close vessel, and leave sesquioxide instead of carbide of iron. (Boudault.) — 3. When mixed with *cupric oxide* and heated, they exhibit a bright glimmering light, and with *nitrate of ammonia* they detonate loudly. (Gm.) When this salt is thrown into melted nitrate of ammonia, a dark-blue mass is formed, which afterwards turns reddish yellow; as long as it remains blue, the filtered solution forms a blue precipitate with ferric nitrate. (Schönbein.) — 4. Continued *boiling* of the aqueous solution converts only a small portion of the salt into the yellow ferrocyanide. (Gm.)—The dilute solution is permanent in the dark, but, on exposure to *sunshine*, it slowly deposits a reddish yellow substance; paper saturated with the solution, and placed in a bottle exposed to the sun, evolves a slight odour of hydrocyanic acid, and turns blue when treated with sesquichloride of iron. (Schönbein, *Pogg.* 67, 89.) — 5. In the circuit of the voltaic battery, that part of the solution which is in contact with the negative pole, acquires the property of colouring ferric salts blue; hence ferrocyanide of potassium is formed at that pole. (Schönbein.) [Is free cyanogen, together with a cyanide of iron, separated at the positive pole?]

6. Chlorine gas passed through the aqueous solution, eliminates chloride of cyanogen; and precipitates prussian green, while choride of potassium remains in solution. The solution acquires a dark red colour from dissolved prussian blue [prussian green], which may be precipitated by alkaline salts; alkalis likewise change the red colour to yellow. (Smee.) Chlorine separates hydrocyanic acid from the solution as well as chloride of cyanogen, and imparts to it a dark-red colour arising from dissolved prussian green, which is precipitated by exposure to the air, or by boiling.

(Pelouze, *Ann. Chim. Phys.* 69, 40.)—*Bromine* acts on the aqueous solution in the same manner as chlorine. (Smee.) — 7. *Nitric acid* forms with the crystals, gradually even at ordinary temperatures, a brown solution identical with that which it produces with the yellow ferrocyanide (p. 461); it likewise deposits crystals of nitre (Gm.), and contains nitroprusside of potassium. (Playfair.) — 8. The pulverized crystals heated with *oil of vitriol* become pale yellow, and impart that colour to the oil of vitriol (sulphate of ferricyanide of potassium ?); at a higher temperature, the mass becomes bluish-white and tough (sulphate of ferrocyanide of potassium ?); at a still higher temperature, it swells up and evolves combustible gases, and, finally, at a red heat, leaves a residue of sulphate of ferric oxide and potash. (Gm.)—Oil of vitriol forms with the aqueous solution a green precipitate, which consists of Fe^2Cy^3 [?] mixed with a small quantity of cyanide of potassium, and turns blue when boiled with excess of sulphuric acid, part of the cyanogen being thereby converted into ammonia. (Williamson, *Ann. Pharm.* 57, 243.)—Ferricyanide of potassium mixed with *sulphate of ammonia* and with water, and evaporated to the consistence of paste, forms a green mass, which, if further heated nearly to its melting point, assumes a deep blue colour, and when subsequently dissolved in water, yields a filtrate, which does not form a blue precipitate with ferric salts. (Schönbein.) — 9. The aqueous solution of the red salt boiled with hydrochloric acid, deposits prussian blue. (Gm.)—Most acids produce this precipitation on the application of heat, and generally also give rise to evolution of hydrocyanic acid. (Smee.) If the solution likewise contains the yellow ferrocyanide, evaporation with hydrochloric acid produces a large quantity of prussian blue. (Gm.)—This reaction is probably attended with evolution of cyanogen :

$$3(3KCy,Fe^2Cy^3) + 10HCl = 2Cy + 10HCy + 9KCl + FeCl + Fe^5Cy^6.$$

On adding to the boiling solution of the red salt, a quantity of protochloride of iron not sufficient for complete precipitation, the yellow ferrocyanide is formed, and prussian blue B precipitated (Liebig, *Ann. Pharm* 57, 237):

$$2K^3Fe^2Cy^6 + 4FeCl = 4KCl + K^2FeCy^3 + Fe^7Cy^9.$$

10. When the aqueous solution of ferricyanide of potassium is boiled with mercuric oxide, the whole of the iron is precipitated in the form of pulverulent ferric oxide, to which small quantities of potassium and cyanogen tenaciously adhere (Gm.):

$$K^3Fe^2Cy^6 + 6HgO = 3KO + Fe^2O^3 + 6HgCy.$$

11. *Potash* does not act on the solution at ordinary temperatures, nor even at higher temperatures, unless the liquid be boiled down to a high state of concentration; in that case, the red prussiate is converted into the yellow prussiate and cyanide of potassium, with evolution of cyanogen (not of oxygen) and precipitation of ferric oxide. (Boudault.)

12. Many *heavy metallic oxides*, in presence of potash, convert the dissolved red prussiate into the yellow prussiate, the red salt taking up potassium, and the oxygen of the potash bringing the heavy metal to a higher state of oxidation (Boudault, *N. J. Pharm.* 7, 437; also *J. pr. Chem.* 36, 23); *e.g.*

$$K^3Fe^2Cy^3 + KO + PbO = 2K^2FeCy^3 + PbO^2. \text{ (Boudault.)}$$

The action may be produced by adding to the solution of the red salt,

either the hydrated oxide together with potash, or a mixture of the salt of the heavy metal with excess of potash.—A solution of *chromic oxide* in potash boiled with the solution of the red salt, yields chromate of potash, together with ferrocyanide of potassium.—*Hydrated manganous oxide* with potash, or a manganous salt with excess of potash, yields peroxide of manganese, even at ordinary temperatures; if the potash is in large excess, the peroxide produced is crystalline; but if the manganous oxide is in larger proportion, brown-red manganoso-manganic oxide is produced.—*Protoxide of lead* dissolved in potash, or a lead-salt supersaturated with potash, yields a precipitate of brown peroxide of lead, which is generally crystalline, or of red lead, if the lead-oxide is present in greater proportion.—*Stannous salts* also convert the red salt mixed with potash into the yellow salt.—But the *protoxides of cobalt and nickel* are not brought to a higher state of oxidation even by boiling with a mixture of potash and the red salt.—*Silver* and *gold salts*, on the other hand, exhibit a different reaction with potash and the red prussiate; for they yield, on boiling, a precipitate of ferric oxide, while ferrocyanide of potassium and cyanide of silver and potassium, or cyanide of gold and potassium, remain in solution.

13. *Hydrosulphuric acid* decomposes the red prussiate dissolved in water into yellow prussiate, ferroprussic acid, and sulphur (Williamson, *Ann. Pharm.* 57, 237):

$$2K^3Fe^2Cy^6 + 2HS = 3K^2FeCy^3 + H^2FeCy^3 + 2S.$$

14. *Hydroselenic acid* and *phosphuretted hydrogen* likewise impart to the solution of the red prussiate the property of forming a blue precipitate with ferric salts; and the same change is produced, though more slowly, by *hydrotelluric acid*, *arseniuretted hydrogen*, and *antimoniuretted hydrogen* gases. (Schönbein.)

15. *Ammonia* converts the aqueous solution of ferricyanide of potassium into ferrocyanide of potassium and ferrocyanide of ammonium, with evolution of nitrogen (Monthiers, *N. J. Pharm.* 11, 254):

$$6K^3Fe^2Cy^6 + 8NH^3 = 9K^2FeCy^3 + 3[(NH^4)^2FeCy^3] + 2N.$$

Many other deoxidizing agents likewise impart to the aqueous solution of ferrocyanide of potassium the property of forming a blue precipitate with ferric salts, and consequently, when added to a mixture of the red solution with a ferric salt, they produce an immediate precipitation of prussian blue. Whether in this reaction ferrocyanide of potassium is invariably produced, or whether some of these bodies merely reduce the ferric salt previously or subsequently added, to the state of ferrous salt, so that the blue precipitate may be produced by the red prussiate in its original state, is a question which has not been satisfactorily investigated. The other decomposition-products formed at the same time likewise require examination. The deoxidizing agents which produce these effects are: *Phosphorus*, which acts but slowly. (Schönbein, *J. pr. Chem.* 30, 128.)—*Phosphorous acid* and the *hypophosphites*. (Boudault, *N. J. Pharm.* 7, 437; also *J. pr. Chem.* 36, 12.)—*Sulphurous acid*, which is thereby converted into sulphuric acid, and *Sulphites*, which are transformed in sulphates. (Boudault.) *Nitric oxide gas*, and even fuming nitric acid, whereas nitrous oxide and pure nitric acid exert no reducing action. (Schönbein.)

Similar effects are likewise produced by various metals: *Iron* sus-

pended in the solution soon becomes covered on the rough parts of its surface with blue cyanide of iron, which grows up in capillary or feathery forms to the very surface of the liquid, and there acquires a dark blue colour. On boiling the solution of the red prussiate with iron, a precipitate is formed, which is first bluish-green, then green, then pale green, then grey, and finally whitish-grey, and acquires a dark blue colour on exposure to the air. The solution is thereby nearly decolorized, becomes somewhat alkaline, and contains ferrocyanide of potassium. (Hünefeld, *J. pr. Chem.* 7, 23.) Iron quickly becomes covered with a light blue substance, changing to dark blue on exposure to the air, and imparts to the solution the property of forming a blue precipitate with ferric salts. The formation of the blue deposit requires the presence of air; for iron wire introduced into the boiling solution remains bright, if the liquid be left to cool out of contact with the air; but if the air be not completely excluded, blue spots form upon the iron in the course of two days, and gradually increase to long, thin, spiral threads of a dirty blue colour, which gradually grow up to the stopper. At length the solution becomes decolorized, and precipitates ferric salts dark blue, and ferrous salts white. (Schönbein.)—*Zinc* acts nearly as rapidly as iron, becoming covered with yellowish white spots and depositing a dirty-white powder. The solution at first yields a blue precipitate with ferric salts; but after the action has been continued for some time, the liquid becomes decolorized, no longer precipitates ferric salts blue, and contains abundance of ammonia. In a solution freed from air by boiling, zinc remains bright for weeks, while the solution retains its colour, and imparts but a slight blueness to ferric salts. (Schönbein.)—*Arsenic, antimony, bismuth, tin*, and *lead*, quickly impart to the solution the property of turning ferric salts blue; *cadmium, copper, mercury*, and *silver*, produce the same effect but very slowly. But even on *gold, platinum* and *palladium*, a mixture of the red prussiate solution with ferric nitrate deposits prussian blue in a few hours. (Schönbein.) [But this mixture deposits prussian blue even when left by itself for some time in a glass. (Gm.)] Finely divided *stannous* or *cuprous oxide* added to a solution of the red prussiate, quickly produces a small quantity of the yellow salt. (Schönbein.)

Iodide of potassium, added to a mixture of the solution with a ferric salt, likewise causes a precipitation of prussian blue. (Smee.) [The action is probably attended with elimination of iodine.]

Certain *organic substances* likewise impart to the solution of the red prussiate the property of forming a blue precipitate with ferric salts: *Uric acid, creosote, cinchonine* and *morphine* (but not quinine or strychnine), produce this change in a minute.—*Ether* or *alcohol* exerts no action on the pure solution, even after long standing; but if it be mixed with ferric nitrate (which by itself is not reduced by alcohol or ether), a copious precipitate of prussian blue is quickly formed. Boiling for a short time with *sugar* imparts but little blueing power to the pure solution; but from the solution mixed with a ferric salt, sugar throws down prussian blue in a few hours, even at ordinary temperatures. (Schönbein.) *Formic acid* mixed with the pure solution of the red prussiate, and set aside for a few days, or evaporated with it, causes a slight precipitation of prussian blue, and imparts to the solution the power of forming a blue precipitate with ferric nitrate. Similar effects are produced by *acetic, tartaric*, and *citric acid*. But oxalic acid exhibits no action even on boiling; on the contrary, the addition of oxalic acid in considerable quantity to a mixture of the red prussiate and ferric nitrate

entirely prevents the precipitation of prussian blue by hyponitric acid, nitric oxide, sulphuretted hydrogen, phosphuretted hydrogen, uric acid, or sugar, and diminishes the precipitate which would be formed by seleniuretted hydrogen. (Schönbein.) If, however, the solution of the red salt be mixed with potash, the oxalic acid is decomposed by it, with formation of carbonate of potash and ferrocyanide of potassium. (Boudault.) ¶ A piece of cotton coloured with indigo, and saturated with ferricyanide of potassium, is bleached on immersion in caustic potash-ley. (Mercer, *Phil. Mag. J.* 31, 126.) ¶

16. Ferricyanide of potassium in solution does not precipitate the salts of the other alkalis, but forms precipitates with most *salts of the heavy metals*. The reaction which takes place in these precipitations is in most cases expressed by an equation like the following:

$$3KCy,Fe^2Cy^3 + 3(CuO,SO^3) = 3CuCy,Fe^2Cy^3 + 3(KO,SO^3).$$

But in this case also, the new compound frequently carries down with it a quantity of undecomposed ferricyanide of potassium, which it is difficult or impossible to remove by washing. The resulting precipitate is generally resolved by digestion with aqueous potash into reproduced ferricyanide of potassium and separated metallic oxide.

Combinations. Ferricyanide of potassium dissolves in 3·8 pts. of cold and a smaller quantity of hot water. (Gm.) In 2 pts. of cold and less than 1 pt. of hot water. (Girardin.) The saturated solution has a brownish yellow, the dilute solution a lemon-yellow colour, which does not disappear till a very large quantity of water has been added. Alcohol added to the aqueous solution throws down the salt in the form of a yellow powder. (Girardin.)

Ferricyanide of potassium appears to combine with oil of vitriol (p. 471).

It is insoluble in absolute alcohol, and very sparingly soluble in hydrated alcohol. (Gm.)

Ferrocyanide of Iron and Potassium.

$$C^6N^3Fe^2K = C^6N^3FeK^2,C^6N^3Fe^3 = KFe^2Cy^3 = K^2FeCy^3,3FeCy.$$

Ferrocyaneisenkalium (Williamson), *Prussemertepat* (Gm.).—The formation of this salt by heating ferrocyanide of potassium with dilute sulphuric acid, was first pointed out by Everitt (*Phil. Mag. J.* 6, 97).

1. When hydrocyanic acid is prepared by distilling ferrocyanide of potassium with dilute sulphuric acid (pp. 390—392), this compound remains in the retort in the form of a yellow powder, which must be washed out of contact of air, with water previously deprived of air by boiling (Everitt):

$$2K^2FeCy^3 + 6SO^3 + 3HO = 3(KO,2SO^3) + 3HCy + KFe^2Cy^3.$$

The compound obtained from 368·8 pts. (2 At.) of anhydrous ferrocyanide of potassium by sulphuric acid, contains 38 pts. (nearly 1 At.) of potassium. (Williamson.)

The compound is not yellow but white, at least if only 3 At. sulphuric acid are used, so that neutral sulphate of potash is produced. Chlorine

water and hot nitric acid, which withdraw potassium but no iron from it, convert it into the blue compound described on page 477:

$$K^2FeCy^3,3FeCy - K = KFe^2Cy^3,Fe^2Cy^3.$$

The compound also turns blue on exposure to the air, ferrocyanide of potassium being likewise separated. By caustic potash, it is converted into ferrocyanide of potassium, and a residue of ferrous oxide (Williamson):

$$K^2FeCy^3,3FeCy + 2KO = 2K^2FeCy^3 + 2FeO.$$

6 C	36·0	.....	20·78
3 N	42·0	.....	24·25
2 Fe	56·0	.....	32·34
K	39·2	.....	22·63
$C^6N^3Fe^2K$	173·2	.....	100·00

Gay-Lussac (*Ann. Chim. Phys.* 46, 76) thought that he had found in this white substance the compound $K^2Fe^7Cy^9$; but he subsequently discovered (*Ann. Chim. Phys.* 51, 370) that the water which he had used to wash it contained carbonate of lime.

If 100 parts of ferrocyanide of potassium are distilled with 12 parts of oil of vitriol and 20 parts of water till 16 parts of liquid have passed over, and the residue is thoroughly washed with water, the last wash-water exhibits on opalescent appearance, and imparts a violet colour to ferric salts if it still produces a slight cloud with chloride of barium, but colours them dark blue in the contrary case. If the residue, which during this washing has assumed a light blue colour, be gently ignited in contact with the air, and then digested in water, the water takes up ferrocyanide of potassium having a slight alkaline reaction, together with a small quantity of sulphate of potash, and leaves a black mixture which, when treated with hydrochloric acid, gives off hydrogen gas, with a trace of sulphuretted hydrogen; but after strong ignition in the air, the water extracts ferrocyanide of potassium having a strong alkaline reaction, together with a trace of sulphate of potash, and leaves iron mixed with a considerable quantity of sulphide of iron. Hence the light blue residue is a compound of cyanide of iron with ferrocyanide of potassium and sulphate of potash. If the light blue residue be digested with aqua-regia till it becomes dark blue, the resulting yellow liquid contains a certain quantity of ferric oxide, but no sulphuric acid. It it be then thoroughly washed, the greenish yellow wash-water contains ferricyanide of potassium, and the washed prussian blue, when ignited, yields neither ferrocyanide of potassium, sulphate of potash, metallic iron, nor sulphide of iron. (Wackenroder, *N. Br. Arch.* 29, 47.)

2. To this head properly belongs also the white precipitate obtained by mixing a ferrous salt with ferrocyanide of potassium; this precipitate, as shown by Proust, Robiquet, and Berzelius, is not pure protocyanide of iron, but likewise contains ferrocyanide of potassium:

$$2K^2FeCy^3 + 2FeCl = 2KCl + K^2FeCy^3,3FeCy.$$

To obtain this precipitate perfectly white, and not coloured by prussian blue, the ferrous salt must be perfectly free from admixture of ferric salt; the aqueous solution of ferrocyanide of potassium must be thoroughly freed from air by boiling, and the air must be excluded as completely as possible during the mixing. The solution of ferrous sulphite and hypo-

sulphite obtained by immersing iron in aqueous sulphurous acid contained in a close vessel (V., 235), forms with ferrocyanide of potassium, a perfectly white precipitate. (R. Phillips, *Phil. Mag. Ann.* 1, 72.) The same end may be attained by adding sulphurous acid or sulphuretted hydrogen to the ferrous salt.

The precipitate retains potassium, even after long-continued washing with water containing sulphuretted hydrogen and hydrochloric acid, unless it has turned blue by contact with air. (Robiquet.) Ferrous sulphate and ferrocyanide of potassium precipitate one another completely, when 12 parts of the latter are mixed in solution either with 9, 10, or 11 parts of the former; for the liquid above the precipitate exhibits no turbidity, either with ferric salts or with ferrocyanide of potassium. But the precipitate obtained with 9 pts. of green vitriol, gives up ferrocyanide of potassium to the water with which it is washed; that obtained with 11 parts of green vitriol, yields green vitriol; but that obtained with 10 parts of green vitriol, does not yield either salt. (Robiquet.)

The white precipitate is converted by the action of the air and other oxidizing agents into prussian blue. On exposure to the air, it assumes a blue colour continually increasing in depth, and in the same proportion gives up to the wash-water a continually greater quantity of ferrocyanide of potassium, producing an otherwise neutral solution. The abstraction of the potassium is not complete till the precipitate is entirely converted into prussian blue by washing it with water containing air; and as the washing is generally discontinued before this complete conversion is attained, it follows that commercial prussian blue generally contains ferrocyanide of potassium. If an excess of ferrocyanide of potassium has been used in the formation of the white precipitate, the latter, when washed with water containing air, begins to dissolve in it; if it be then washed with water containing hydrochloric acid, which is not coloured by it, till the wash-water leaves no residue on evaporation, and then again with pure water, the wash-water again exhibits a blue colour. (Robiquet, *Ann. Chim. Phys.* 44, 279; compare also Berzelius and Robiquet, p. 440.)

The theory of this prussian blue formation by the action of the air has not yet been satisfactorily made out. The simplest assumption would be that part of the iron is separated by the air in the form of sesquioxide, so that after washing with water, there remains a mixture of prussian blue and ferric oxide:

$$6KFe^2Cy^3 + 3O = 3K^2FeCy^3 + Fe^7Cy^9 + Fe^2O^3.$$

A less probable supposition is that red prussiate, yellow prussiate, and caustic potash are produced, and taken up by the water:

$$24KFe^2Cy^3 + 13O = K^3Fe^3Cy^6 + 4K^2FeCy^3 + 6Fe^7Cy^9 + 13KO.$$

In that case, however, the wash-water should be alkaline from the presence of potash, a fact which is denied by Robiquet.

The white precipitate placed in the circuit of the voltaic battery turns blue at the positive pole. (Schönbein.)—It turns blue in contact with chlorine-water or with nitric acid. It turns blue in contact with chromic acid, or with bichromate of potash (but not with monochromate); also in contact with peroxide of lead or manganese, but only in presence of an acid, such as sulphuric acid. It likewise turns blue immediately when a ferric salt is poured upon it, that salt being thereby converted into ferrous salt (Schönbein):

$$3KFe^2Cy^3 + 2Fe^2Cl^3 = 3KCl + 3FeCl + Fe^7Cy^9.$$

An aqueous solution of red prussiate of potash likewise converts it into prussian blue, with formation of yellow prussiate. (Schönbein, *J. pr. Chem.* 30, 150.) In this case, prussian blue A is probably formed:

$$3KFe^2Cy^3 + K^3Fe^2Cy^6 = 3K^2FeCy^3 + Fe^4Cy^6.$$

Ferricyanide of Iron and Potassium. $C^6N^3Fe^3K,C^6N^3Fe^3=KFe^4Cy^6$.

WILLIAMSON. (*Ann. Pharm.* 57, 228.)

Prussëmert-Prussemertepat. (Gm.)

The white compound KFe^2Cy^3, just considered (pp. 474—476), is converted into this blue substance when treated with chlorine, nitric acid, or sulphuric acid. 1 pt. of the white compound is digested in a basin with 1 pt. nitric acid and 20 pts. water, the liquid being constantly stirred. As the temperature approaches the boiling-point, the compound begins to turn blue and nitric oxide is evolved; as soon as this evolution of gas becomes rapid, the basin must be removed from the fire; the gas however continues to escape till the solid compound has assumed a deep blue colour. If the colour be not deep enough, the compound must be again heated with fresh nitric acid, till a sample decomposed by caustic potash no longer leaves ferroso-ferric but pure ferric oxide. The product is then to be washed till the wash-water no longer leaves a residue of nitre on evaporation.—If the action of the nitric acid has been too strong, the resulting blue compound when treated with potash yields the red instead of the yellow prussiate, and is then useless.

When dry, it exhibits a very beautiful violet colour, with scarcely any coppery lustre. The recently precipitated compound, suspended in water, appears green by transmitted light.

	Dried at 100°.			Williamson.
24 C	144·0	....	20·71	..... 21·11
12 N	168·0	....	24·16	
2 K	78·4	....	11·27	..... 10·75
8 Fe	224·0	....	32·21	..... 32·45
9 HO	81·0	....	11·65	..... 11·41
$2KFe^4Cy^6,9HO$	695·4	....	100·00	

May also be regarded as KFe^2Cy^3,Fe^2Cy^3, that is to say, as ferricyanide of potassium in which 2K are replaced by 2Fe (Williamson), or as prussian blue A in which 1Fe is replaced by 1K.

By further boiling with nitric acid, this blue compound is converted into a dark green substance, which appears to be identical with Pelouze's ¼-cyanide of iron. It is decomposed by aqueous potash, yielding ferrocyanide of potassium and 25·5 per cent. of ferric oxide. [The calculated quantity is 23 per cent.]

$$KFe^4Cy^6 + 3KO = 2K^2FeCy^3 + Fe^2O^3.$$

An excess of the blue compound heated with aqueous solution of yellow prussiate of potash, converts the latter into the red prussiate. If the yellow prussiate is in excess, and the heating is continued for some time, the

blue compound is converted into a pale blue powder containing $1\frac{1}{2}$ times as much potassium as the original substance (Williamson):

$$K^2Fe^5Cy^{12} + 2K^2FeCy^3 = K^3Fe^2Cy^6 + K^3Fe^5Cy^{12}.$$

This blue powder $K^3Fe^5Cy^{12}$ may be regarded as a compound of KFe^4Cy^5 with $2KFe^2Cy^3$, or of 1 At. ferricyanide of potassium with 6 At. protocyanide of iron $= K^3Fe^2Cy^6 + 6FeCy$.

Ferrocyanide of Sodium. $Na^2FeCy^3 = C^6N^3FeNa^2$.

Ferroprussiate of Soda, Hydrocyanate of Ferrous Oxide and Soda; Einfach-Cyaneisennatrium, Eisenblausaures Natron, blausaures Eisenoxydul Natron.

Generally obtained by adding prussian blue to caustic soda-solution as long as the blue colour is thereby changed to brown,—then filtering and crystallizing.—The anhydrous compound has not been studied. The crystals are pale yellow, transparent, rhombic and hexagonal prisms, sometimes with dihedral, sometimes with four-sided summits,—or needles. (John.) Shining, very brittle. Belong to the oblique prismatic system. (*Fig.* 115°); $u' : u = 99° 40'$; $u : t = 139° 50'$; $u : m = 130° 10'$; $i : t = 136° 48'$; $f : t = 128° 37'$; a : a *backwards* $= 104° 8'$; $a : i = 127° 40'$; $a : m = 127° 56'$; no cleavage-planes. (Bunsen, *Pogg.* 36, 413.) Sp. gr. 1·458. Taste slightly saline and bitter.—In warm dry air, the salt effloresces to a white powder, soluble in $4\frac{1}{2}$ pts. of cold water (in 1 pt. according to Ittner), in a smaller quantity of boiling water, but insoluble in alcohol. (John, *N. Gehl.* 3, 171.)

	Crystallized.			Berzelius.		Or:			Ittner.
6 C	36·0	....	13·82			2 NaO....	62·4	.... 23·96	 23
3 N	42·0	....	16·13			FeO	36·0	.... 13·82	 32
Fe	28·0	....	10·75			3 HCy....	81·0	.... 31·11	
2 Na	46·4	....	17·82					....	
12 HO	108·0	....	41·48	....	39	3 HO	81·0	.... 31·11	
$Na^2FeCy^3,12HO$	260·4	....	100·00				260·4	.... 100·00	

Ferricyanide of Sodium. $3NaCy,Fe^2Cy^3 = C^6N^3Na^3,C^6N^3Fe^2$.

Prepared by passing chlorine gas through the aqueous solution of ferrocyanide of sodium, till the liquid no longer gives a blue precipitate with ferric salts—evaporating—filtering, to separate prussian blue and a yellow powder—again evaporating the solution till it crystallizes, and purifying the crystals by recrystallization. (Kramer, *J. Pharm.* 15, 98.)—Or the liquid, after being treated with chlorine, may be concentrated by evaporation, and mixed with alcohol, which accelerates the purification; the alcoholic filtrate, which is yellowish green by reflected, but red by transmitted light, left to evaporate spontaneously; the crystals dissolved in water, and the solution mixed with alcohol again left to evaporate. (Bette, *Ann. Pharm.* 23, 117.)

Ruby-coloured, right four-sided prisms, with truncated lateral edges, and yielding an orange-yellow powder. (Bette.) Green, transparent, four-sided prisms, efflorescent, and melting at 50°. (Kramer.) [Did Kramer's salt contain more water of crystallization?]

The crystals decrepitate when heated, acquire a green colour, fuse with strong decrepitation, but are not completely decomposed even by long-continued ignition. When digested for some time with aqua-regia, they form a brown solution. This salt, when its powder is heated with oil of vitriol, behaves like the corresponding potassium-salt (p. 47), exhaling a peculiar odour, becoming pale yellow, and then bluish white and viscid, and finally giving off a large quantity of gas, and leaving a residue of sulphate of ferric oxide and soda. (Bette.)—The salt deliquesces in the air (Bette); dissolves in 5·3 pts. of cold and 1·25 pts. of boiling water. The yellow solution exhibits a greenish tinge, stronger in proportion to the degree of concentration. (Kramer.) The salt is very sparingly soluble in alcohol (Kramer), but alcohol does not precipitate it from the aqueous solution. (Bette.)

Crystals dried at 100°.				Bette.
3 Na	69·6	....	23·23	..... 22·73
2 Fe	56·0	....	18·69	..... 18·28
6 Cy	156·0	....	52·07	
2 HO	18·0	....	6·01	
$3NaCy,Fe^2Cy^3 + 2Aq.$	299·6	....	100·00	

The water more probably amounts to 3 At.

¶ Ferricyanide of Potassium and Sodium.

$K^3Na^3Fe^4Cy^{12} = 3KCy,3NaCy,2Fe^2Cy^3 = C^6N^3K^3,C^6N^3Na^3,C^{12}N^6Fe^4 = 3KCy,Fe^2Cy^3 + 3NaCy,Fe^2Cy^3.$

When a mixture of the ferricyanide of potassium and sodium is dissolved in water, and the solution abandoned to spontaneous evaporation, the double ferricyanide is deposited in fine, garnet-coloured, cubic crystals. These crystals are anhydrous; when gently heated in a tube, they decrepitate and crumble to powder, but do not give off any water.—On one occasion, the mixed solution deposited large, black-brown, hydrated crystals having the form of hexagonal prisms, with angles nearly =120°, and rounded at the base; but on redissolving them, the solution yielded crystals of the cubic salt. The hydrated crystals do not give off their water at 100°, but at a somewhat higher temperature the water escapes, and the crystals decrepitate and crumble to powder. (Laurent, *Compt. mensuels*, 1849, 324; abstr. *Jahresber.* 1849, 291.)

Anhydrous.			Laurent.	*Hydrated.*			Laurent.
24 C	144	....	23·6	24 C	144	....	20·1
12 N	168	....	27·6	12 N	168	....	23·4 ....
4 Fe	112	....	18·3 .... 18·7	4 Fe	112	....	15·5 .... 16·5
3 K	117	....	11·3 .... 11·0	3 K	117	....	9·7 .... 10·0
3 Na	69	....	19·2 .... 20·5	3 Na	69	....	16·3 .... 16·4
				12 HO	188	....	15·0 .... 14·5
$3KCy,3NaCy,2Fe^2Cy^3$	610	....	100·0	+ 6Aq.	798		

According to Laurent's equivalents, the formula of the anhydrous salt is $C^3N^2fe,K^{\frac{1}{2}}Na^{\frac{1}{2}}$, and that of the hydrated salt, $C^3N^2fe,K^{\frac{1}{2}}Na^{\frac{1}{2}}$ + Aq. [fe = *Ferricum* = ⅓ . 28]. ¶

Ferrocyanide of Barium. $Ba^2FeCy^3 = C^6N^3FeBa^2$.

1. Prussian blue is added to boiling baryta-water, as long as its blue colour is thereby changed to brown,—after which the liquid is filtered at a boiling heat, and left to crystallize by cooling. (W. Henry, *Schw. J.* 3, 672.) The salt being very sparingly soluble, the residue must be repeatedly boiled with water. The crystals may be purified by recrystallization. (Berzelius.)—2. The aqueous solutions of 211·4 pts. (1 At.) of crystallized ferrocyanide of potassium and considerably more than 244 pts. (2½ At.) of crystallized chloride of barium are mixed at a boiling heat, and the crystalline powder which separates on cooling, again boiled with aqueous chloride of barium. If the chloride of barium be not used in excess, the product is a compound of ferrocyanide of barium with ferrocyanide of potassium. (Duflos, *Schw.* 65, 233.)—3. Ferroprussic acid is saturated with baryta-water or carbonate of baryta, the whole boiled with water, and filtered. (*Berzelius Lehrb.*)

The crystals thus obtained are small, yellow, transparent, rhomboidal parallelopipeds (W. Henry); oblique rectangular prisms. (Bunsen, *Pogg.* 36, 416.) *Fig.* 92; the *m*-face large; the *t*-face small; $i : m = 142° 49'$, $m : t = 90°$. (Bunsen.) They are not decomposed by mere exposure to the air, but at 40° they give off their water and become white and opaque. Of the 6 At. water which these crystals contain, only 5½ At., or 16·56 per cent. (16·59 p. c. according to Porrett), are given off at a heat which they can bear without further decomposition, the remaining ½ At. water being obstinately retained. (Berzelius.) The residue decomposes at a red heat (without fusing, according to Duflos), more readily than ferrocyanide of potassium, into nitrogen gas, cyanide of barium, and carbide of iron. When the ignition takes place in contact with air, the residue consists of ferric oxide and carbonate of baryta. (Berzelius.) 7 parts of the salt boiled for an hour with 10 parts of mercuric oxide and with water, yield a filtrate containing baryta, cyanide of mercury with a small quantity of mercuric oxide, and a residue consisting of ferric oxide, mercurous oxide and mercury. With mercuric sulphate, the barium compound behaves like ferrocyanide of potassium (p. 465). (Duflos, *Schw.* 65, 114.)—The crystals dissolve in 584 parts of cold water, according to Duflos; in 1800, according to Porrett; in 1920, according to Thomson; and in 100 parts of boiling water, according to Thomson; in 116, according to Duflos. Sulphuric acid added to the solution throws down the baryta, leaving ferroprussic acid in solution. (Porrett.) With oil of vitriol, the crystals form—less easily, however, than ferrocyanide of potassium—a solution which, when exposed to a damp atmosphere, yields crystals decomposible by water, the products of the decomposition being sulphate of baryta, ferroprussic acid, and free sulphuric acid. (Berzelius.)—On passing chlorine through the aqueous solution, it becomes turbid, acquires a greenish yellow colour, deposits a green powder, then becomes brown and dark red, and is decomposed on evaporation, depositing a bluish white powder, but yielding no crystals. (Kramer.)

	Crystallized.			Berzelius.
2 Ba	137·2	....	46·16	45·89
Fe	28·0	....	9·43	9·28
3 Cy	78·0	....	26·24	
6 HO	54 0	....	18·17	
$Ba^2FeCy^3 6Aq$	297·2	....	100·00	

Green Ferrocyanide of Barium.—When the yellow salt is prepared by digesting prussian blue with baryta-water, and then filtering and crystallizing, the isomeric green modification remains in the mother-liquid. This solution gives no precipitate with alcohol; with ferric salts it yields prussian blue. When left to evaporate slowly in the air, it deposits small crystals of nitrate of baryta, at the same time losing its green colour; the colour may, however, be restored by pouring alcohol on the dried residue, and exposing it for a while to the sun. (*Berzelius Lehrb.*)

Ferrocyanide of Barium and Potassium. $KBaFeCy^3=K^2FeCy^3,Ba^2FeCy^3$.

Obtained by precipitating a solution of a baryta-salt, not too dilute, with ferrocyanide of potassium. (Mosander, *Pogg.* 25, 390.) The ferrocyanide of potassium must be in excess. (Duflos, *Schw.* 65, 233.) On mixing a boiling solution of 1 pt. crystallized chloride of barium with a solution of 2 pts. crystallized ferrocyanide of potassium, also at a boiling heat, the compound crystallizes out on cooling. (Bunsen, *Pogg.* 36, 416.)

Light yellow crystals. (Duflos.) Slightly obtuse, truncated rhombohedrons, *Fig.* 153; $p : r = 118° 53'$; $r : r^3 = 81° 29'$; r or $r^3 : r^3 = 98° 33'$; cleavage parallel to r. (Bunsen.) The crystals give off 6 per cent. of water when heated in the air, fusing at a red heat, and leaving ferric oxide mixed with potash. (Duflos.) They dissolve in 38 pts. of cold, and 9·5 pts. of boiling water (Duflos); in 36·38 pts. of water at 14°, and in 11·85 of boiling water. (Mosander.)

	Crystallized.			Duflos.
K	39·2	16·28		17·33
Ba	68·6	28·49		30·00
Fe	28·0	11·63		11·90
3 Cy	78·0	32·39		
3 HO	27·0	11·21		
$KBaFeCy^3,3Aq$	240·8	100·00		

Mosander gives the same formula for the crystals.

Ferricyanide of Barium and Potassium. KBa^2Cy^3,Fe^2Cy^3.

Chlorine gas is passed through the aqueous solution of the preceding salt, till it retains the odour of chlorine after agitation; the excess of chlorine is expelled by heat; a small quantity of alcohol added; the liquid filtered from the prussian blue, and left to evaporate; the larger crystals of the double ferricyanide separated from the needles of ferricyanide of potassium which attach themselves to them; and lastly, purified by recrystallization. Short six-sided prisms composed of lamellæ radiating from a centre. Reddish black, but exhibit a dark-red colour by transmitted light when in thin laminæ; yield a brownish yellow powder; permanent in the air. The powder when heated bakes together without fusing; gives off hydrocyanic acid and water; dissolves readily in water; and is precipitated from the solution by a large quantity of alcohol. (Bette, *Ann. Pharm.* 23, 138.)

	Crystallized.				Bette.
K	39·2	....	8·86	.....	8·97
2 Ba	137·2	....	31·01	.....	30·54
2 Fe	56·0	....	12·66	.....	12·48
6 Cy	156·0	....	35·26		
6 HO	54·0	....	12·21		
$KBa^2Cy^3,Fe^2Cy^3 + 6Aq.$	442·4	....	100·00		

Ferrocyanide of Strontium. $Sr^2FeCy^3 = C^6N^3FeSr^2$.

A solution of ferroprussic acid in alcohol and water prepared according to 2 (p. 429), is digested with carbonate of strontia till the alcohol is evaporated. The filtrate is then concentrated by evaporation, whereupon a considerable quantity of green matter, probably prussian green, is deposited, and imparts a greenish colour to the crystals; hence they must be purified by repeated solution in water, filtration, and crystallization, till they exhibit a pure yellow colour. (Bette, *Ann. Pharm.* 22, 148.)—W. Henry (*Scher. J.* 3, 674), by digesting prussian blue with strontia-water, and evaporating the filtrate, obtained no crystals, but a white mass, which was not decomposed by exposure to the air. Bette, by digesting prussian blue with carbonate of strontia and water, and then filtering and evaporating, obtained a red substance, probably red prussiate of potash, which sometimes occurs in prussian blue.

Pale yellow rhombic prisms, having their lateral edges deeply truncated. (Bette.) The crystals effloresce readily, turning white, and giving off 21 per cent. (7½ At.) water. When heated in the water-bath, they give off 38·6 per cent. (14 At.) The last atom of water appears to be retained till the temperature rises to the point at which the compound is decomposed. The crystals dissolve in 2 pts. of cold, and less than 1 pt. of boiling water, and are slightly soluble in alcohol. Carbonate of ammonia added to the aqueous solution throws down all the strontia in the form of carbonate. (Bette, *Ann. Pharm.* 22, 148.)

	Crystallized.				
2 Sr	88	....	26·75	.....	26·34
Fe	28	....	8·51	.....	8·36
3 Cy	78	....	23·71		
15 HO	135	....	41·03		
$Sr^2FeCy^3 + 15Aq.$	329	....	100·00		

Ferrocyanide of Calcium. Ca^2FeCy^3.

Formed by boiling pure prussian blue with milk of lime not in excess, exposing the filtrate to the air till the free lime is precipitated in the form of carbonate, and evaporating. (Ittner.) The syrupy solution deposits crystals after a few days. (Berzelius, *Schw.* 30, 12.)

Large pale yellow rhombic prisms, truncated at the obtuse summits. (Berzelius.) Flattened rhombic prisms with a few acumination-faces; $u' : u = 133°$ nearly. (Bunsen, *Pogg.* 36, 416.) They have an unpleasant bitter taste. At 40°, they give off 39·61 per cent. (11½ At.) water, without falling to pieces, and at a higher temperature they give

off water, together with a small quantity of carbonate and hydrocyanate of ammonia; at a heat near redness the residue exhibits a faint glow. The salt when burnt in the air leaves a residue of ferric oxide and carbonate of lime. (Berzelius.) The salt dissolves readily in water (Eug. Marchand); according to Ittner, who however did not obtain it in the crystallized state, it deliquesces even on exposure to the air. It does not dissolve in alcohol.

	Crystallized.			Berzelius.
2 Ca	40	....	15·75	..... 15·95
Fe	28	....	11·02	..... 10·68
3 Cy	78	....	30·71	
12 HO	108	....	42·52	
$Ca^2FeCy^3 + 12Aq$	254	....	100·00	

The following basic compounds, which have not yet been fully examined, also belong to this head:

1. When prussian blue is digested with lime, even in excess, a residue is left, consisting, not of pure ferric oxide, but of a light, ochre-yellow substance. (Berzelius.)

2. When prussian blue is boiled with excess of lime, the filtrate deposits a dark carmine-coloured mass in amorphous laminæ. Boiling potash-ley acting upon this substance forms ferrocyanide of potassium, and leaves a residue of carbonate of lime, which is first white and afterwards blue, and after washing dissolves in hydrochloric acid, forming a transparent and colourless liquid. The red mass boiled with strong nitric acid or aqua-regia yields a clear brown solution, which exhibits with potash and sulphuretted hydrogen the purple colour mentioned on page 461; it is moreover free from copper. (Gm.)

3. When the salt $KCaFeCy^3$ is heated in the air, and then dissolved in water, the solution acquires a bright crimson colour on exposure to the sun (even if it be kept from the air, and potash added to it), but becomes colourless again in the shade. The solution must be alkaline, and must contain still undecomposed ferrocyanide of potassium; but on precipitating it with a copper-salt, the solution loses the power of turning red in the sun, but recovers it on the addition of ferrocyanide of potassium. The reddening is also destroyed by a heat of 50°, but reappears on exposure to the sun after cooling. The red solution evaporated in sunshine leaves a carmine-coloured residue. The reddening cannot be attributed to the cyanate of potash which is formed when the above-mentioned double salt is heated in contact with the air; for even after it has been heated in a covered crucible, the solution of the residue turns red on exposure to the sun. Acids added to the reddened solution sometimes throw down a red, ferruginous powder, which is decolorized by carbonate of potash. (Campbell, *Ann. Pharm.* 28, 54.)

Ferridcyanide of Calcium. $3CaCy,Fe^2Cy^3$.—Obtained by carefully treating the aqueous solution of the ferrocyanide with chlorine.—Fine, aurora-coloured needles, which yield an orange-yellow powder.—When heated to redness in the air, they give off water, hydrocyanic acid, and ammonia, assuming a green colour at the commencement, and leave a residue consisting of ferric oxide and carbonate of lime.—Deliquescent, not precipitated from the aqueous solution by very strong alcohol. (Bette, *Ann. Pharm.* 23, 116.)

	Crystallized.			Bette.
3 Ca	60	....	15·79	15·17
2 Fe	56	....	14·74	14·95
6 Cy	156	....	41·05	
12 HO	108	....	28·42	
$3CaCy,Fe^2Cy^3+12Aq.$	380	....	100·00	

Bette supposes that the crystals contain only 10 At. water.

Ferrocyanide of Calcium and Potassium. $KCaFeCy^3=K^2FeCy^3$, Ca^2FeCy^3.—Formed by precipitating the solution of a lime-salt, not too dilute, with [an excess of] ferrocyanide of potassium; the precipitate gradually increases. (Mosander, *Pogg.* 25, 391.) The calcium is completely precipitated, even when the solution of the lime-salt contains only $\frac{1}{1000}$ pt. of lime, provided the ferrocyanide of potassium be added in great excess. A very dilute solution of gypsum does not indeed yield a precipitate with solution of ferrocyanide of potassium; but if it be saturated hot with crystallized ferrocyanide of potassium, the precipitate is produced; precipitation is likewise produced by a small quantity of ferrocyanide of potassium, provided the mixture be saturated while hot with sal-ammoniac, common salt, or nitre. (Campbell.)—The lime-solution must be quite neutral, because the precipitate is soluble in acids. In hot solutions the precipitation is complete in a moment. (Eug. Marchand, *J. Chim. méd.* 20, 558.)

The yellowish-white precipitate adheres closely to the sides of the vessel. (Marchand.) When dry, it forms a white crystalline powder. (Mosander.) When gently heated and dissolved in water, it yields a liquid which turns red in the sun (*vid. sup.*). When set on fire after drying, it continues to glow till it is converted into ferric oxide, cyanate of lime, and cyanate of potash. (Campbell, *Ann. Pharm.* 28, 53.)—The salt is decomposed by long washing, with formation of metallic ferricyanides and separation of ferric oxide on the surface. It dissolves in nitric acid of sp. gr. 1·2, without any evolution of gas, and forms a dark brown liquid, which becomes red-brown when diluted, and yields no precipitate with ammonia, but a blue precipitate with ferrocyanide of potassium (*comp.* p. 461). It dissolves in dilute hydrochloric acid; concentrated hydrochloric acid precipitates the salt from it unaltered, and potash throws down hydrate of lime. The salt dissolves in 795 pts. of water at 15°, and in 145 pts. of boiling water. The latter solution is yellow, yields no deposit on cooling, gradually acquires a greenish tint, and then forms a precipitate with oxalate of ammonia (which before it did not). (Mosander? *Berzelius Lehrb.*)

	Dried at 70°.			E. Marchand.
K	39·2	....	20·39	20·34
Ca	20·0	....	10·41	10·49
Fe	28·0	....	14·57	15·60
3 Cy	78·0	....	40·58	
3 HO	27·0	....	14·05	
$KCaFeCy^3+3Aq.$	192·2	....	100·00	

According to Mosander, the precipitate is anhydrous.

Ferrocyanide of Magnesium. Mg^2FeCy^3.—By saturating ferroprussic acid with carbonate of magnesia and evaporating the filtrate, small

needles are obtained of a very pale yellow colour, and united in stellate groups. They are permanent in the air, retain their form when ignited, but acquire a deeper yellow colour. They dissolve in 3 pts. of cold water, forming a pale yellow solution, which is only precipitated by carbonate of ammonia or carbonate of soda from hot solutions. (Bette, *Ann. Pharm.* 22, 152; 23, 115.)—By boiling prussian blue with magnesia and water, Ittner obtained deliquescent tables.

	Crystallized.			Bette.
2 Mg	24	....	10·08	11·38
Fe	28	....	11·77	11·89
3 Cy	78	....	32·77	
12 HO	108	....	45·38	
$Mg^2FeCy^3 + 12Aq$	238	....	100·00	

Bette supposes that the crystals contain 10 At. water.

Ferridcyanide of Magnesium.—The solution of the preceding salt treated with chlorine, yields on evaporation a red-brown, non-crystalline mass, which, when heated, gives off hydrocyanic acid without fusing, and afterwards burns like tinder, leaving ferric oxide and magnesia. Gives off hydrocyanic acid when treated with dilute acids; dissolves readily in water, forming a yellowish green liquid, which becomes yellow when very dilute, and is not precipitated by alcohol. It contains 9·57 per cent. of magnesium and 12·85 per cent. of iron.

Ferrocyanide of Magnesium and Ammonium.—Known only in an impure state.—*a. Containing Potassium.* Formed by mixing a solution of a magnesia-salt with a sufficient quantity of sal-ammoniac, then with ammonia, and then with ferrocyanide of potassium. At ordinary temperatures, the precipitate takes several hours to form, but on boiling it appears immediately; it has the form of a heavy white powder, which does not decompose at 100°. When strongly heated in a glass tube, it gives off cyanogen, hydrocyanate of ammonia, together with a small quantity of water, and leaves a black powder, which retains cyanogen even at a strong red heat, and dissolves in 178 pts. of boiling water, forming a yellow solution, which has a disagreeably saline taste.

b. Containing Calcium. Formed by using ferrocyanide of calcium in the precipitation instead of the potassium-salt. The white precipitate has a tinge of peach-blossom colour, and when dry, is not so loose and light as *a*. (Bunsen, *Pogg.* 34, 142.)

The following analyses by Bunsen do not admit of any stoichiometrical calculation, probably because the precipitates are mixtures. The precipitate *b* is most nearly represented by the formula: $NH^4MgFeCy^2 + Aq$.

a.		*b.*	
NH^3	9·43	NH^3	10·84
K	4·81	Ca	2·25
Mg	9·91	Mg	8·47
Fe	17·44	Fe	17·30
Cy	55·27	Cy	54·03
HO	3·14	HO	7·11
	100·00		100·00

Ferrocyanide of Magnesium and Potassium. $KMgFeCy^3$.—A solution of sulphate of magnesia, not too dilute, gradually yields this precipitate when mixed with excess of ferrocyanide of potassium. (Mosander, *Pogg.* 25, 391.)—Even very dilute solutions of magnesia-salts form with ferrocyanide of potassium, especially when heated, a copious yellowish white precipitate which adheres closely to the sides of the vessel, and is soluble in acids. (E. Marchand, *J. Chim. méd.* 20, 558.)—White granular precipitate, which, after drying, forms a loose anhydrous powder. When washed in the air, it is decomposed in the same manner as the corresponding calcium-compound. Dissolves in 15·75 parts of water at 15°, and in 238 pts. of boiling water; the latter solution is yellow, deposits nothing on cooling, and soon turns greenish on exposure to the air. (Mosander? *Berzelius Lehrb.*)

Ferrocyanide of Cerium.—Ferrocyanide of cerium forms with cerous salts a white precipitate, soluble in nitric acid, but not yet further examined.

Ferrocyanide of Yttrium.—Formed by precipitating hydrochlorate of yttria (the acetate, according to Berzelius, yields no precipitate) with ferrocyanide of potassium; the white precipitate changes after a while to pearl-grey. (Eckeberg.) It has the same composition, viz., Y^2FeCy^3, whether the yttria-salt or the ferrocyanide of potassium be in excess. It is not decomposed in drying, merely acquiring thereby a tinge of sea-green. It is but very slowly decomposed by ignition. (Berlin.) It is decomposed by caustic potash into yttria and ferrocyanide of potassium, and does not dissolve either in water or in acetic acid. (Eckeberg.) It is soluble in hydrochloric acid. (Klaproth.)

Ferrocyanide of Glucinum.—By digesting ferrocyanide of lead with aqueous disulphate of glucina, then filtering and evaporating, a transparent varnish is obtained, easily soluble in water, and often exhibiting a bluish tinge, arising from incipient decomposition. (Berzelius, *Ann. Chim. Phys.* 15, 240.)

Ferrocyanide of Aluminum ?—a. Aqueous ferroprussic acid saturated with hydrate of alumina forms a sparingly soluble—or if combined with a smaller quantity of the earth, an easily soluble—compound, which is for the most part decomposed by evaporation. (Berzelius.)

b. Ferrocyanide of lead digested with aqueous sulphate of alumina, forms an insoluble compound, surmounted by nearly pure water. (Berzelius.)

Salts of alumina mixed with ferrocyanide of potassium eliminate hydrocyanic acid, and form a green precipitate, changing to blue, and consisting of hydrate of alumina mixed with cyanide of iron. (Ittner.) A solution of alum is not clouded by ferrocyanide of potassium (Berzelius); only when heated. (Gm.)

Ferrocyanide of Thorinum.—Ferrocyanide of potassium forms with neutral thorina-salts, a heavy white powder, soluble in acids, insoluble in water, and decomposed by potash, with separation of thorina. (Berzelius, *Pogg.* 16, 406.)

Ferrocyanide of Titanium.—Ferrocyanide of potassium forms with salts of titanic oxide a thick yellowish brown precipitate (dark green, if it contains iron).—Carbonate of potash decomposes it, with separation of titanic oxide in the form of a white mass. (Herschel, *Pogg.* 25, 627.)

Ferrocyanide of Tantalum.—Aqueous ferrocyanide of potassium forms a yellow precipitate with tantalic acid dissolved in acid oxalate of potash. (Wollaston.) It converts solid chloride of tantalum into a brownish yellow substance, which becomes dark brown after washing and drying, and is not altered by air and boiling water. (Berzelius, *Pogg.* 4, 14.)—This compound is not precipitated on adding solution of ferrocyanide of potassium to chloride of tantalum previously moistened with water, or to a solution of tantalic acid in aqueous hydrofluoric acid. (Berzelius.)

Ferrocyanide of Molybdenum.—*a. Salts of Molybdous oxide* form with ferrocyanide of potassium a dark brown precipitate, which dissolves in excess of the ferrocyanide, and likewise in ammonia, forming dark-brown solutions. The latter solution deposits the greater part of the compound on the addition of sal-ammoniac, retaining however a faint purple colour. (Berzelius, *Pogg.* 6, 379.)

b. Salts of Molybdic oxide form with ferrocyanide of potassium a dark-brown powder, insoluble in excess of the ferrocyanide. Ammonia dissolves the powder after washing, but in a decomposed state, as molybdic oxide and ferrocyanide of ammonium, the former of which may be precipitated from the aqueous solution by sal-ammoniac. (Berzelius, *Pogg.* 6, 349.)

c. With a solution of *Molybdic acid* in the stronger acids, ferrocyanide of potassium forms a red-brown precipitate, paler than that of *a* or *b*. This precipitate dissolves in excess of ferrocyanide of potassium, forming a dark red-brown solution, and very easily, without colour, in aqueous ammonia, in the form of ferrocyanide of ammonium and molybdate of ammonia. (Berzelius, *Pogg.* 6, 385.)

Cyanides of Iron and Vanadium.—*a. Salts of Vanadic oxide* form with *Ferrocyanide* of potassium a bulky, lemon-yellow precipitate, which persistently colours the wash-water yellow, acquires while drying in the air, first a greenish and then a green colour, and does not dissolve perceptibly in acids. (Berzelius.)

b. With *Ferridcyanide* of potassium, *salts of Vanadic oxide* form a green, gelatinous precipitate. (Berzelius.)

c. Ferrocyanide of potassium added to a solution of *Vanadic acid* in the stronger acids, throws down beautiful green flakes, insoluble in acids. The same compound, only basic, is produced by exposing *a* to the air. (Berzelius, *Pogg.* 22, 26 and 39.)

Cyanides of Iron and Chromium.—*a.* Cr^2FeCy^3?—Ferrocyanide of potassium forms a yellow precipitate with protochloride of chromium. (Péligot.)

b. $3FeCy,Cr^2Cy^3$?—Sesquicyanide of chromium and potassium forms a brick-red precipitate with ferrous salts; none with ferric salts. (Böckmann.)

Salts of chromic oxide are not precipitated by ferricyanide of potassium in any proportion; but on adding sal-ammoniac to the mixture and evaporating over the water-bath, hydrocyanate of ammonia is evolved, and there remains a dark-green gelatinous mass, which, when thoroughly washed with water, leaves a dark-green, tumefied compound of sesquicyanide of chromium with protocyanide of iron. This compound dries up to a nearly black mass, which has a conchoidal fracture and yields

a dark-green powder. With acids it forms a green solution, from which ether separates ferroprussic acid. (*Berzelius Lehrb.*)

Compound of this salt with Ferrocyanide of Potassium.—Formed by adding alcohol to the aqueous mixture of ferrocyanide of potassium and sesquichloride of chromium, the latter somewhat in excess, and washing the resulting dark-yellow, semi-crystalline precipitate with alcohol. The precipitate effloresces during desiccation, and becomes lighter in colour. Water extracts from it ferrocyanide of potassium, together with a small quantity of the compound of sesquicyanide of chromium and protocyanide of iron, leaving undissolved a compound containing a much smaller proportion of ferrocyanide of potassium. (*Berzelius Lehrb.*)

Cyanides of Iron and Uranium.—*a.* U^2FeCy^3 ?—Ferrocyanide of potassium forms with aqueous protochloride of uranium a light brown precipitate, which dissolves readily, but with decomposition, in hot aqua-regia, sparingly in hydrochloric or nitric acid, and is resolved by potash-ley into uranous oxide and ferrocyanide of potassium. (Rammelsberg, *Pogg.* 59, 12.)

b. $2U^2O^2Cy,FeCy$?—Uranic salts form with ferrocyanide of potassium a thick, dark, brown-red precipitate (flocculent, according to Lecanu, if the acid is not in excess). It is coloured yellow by ammonia or carbonate of ammonia, and then dissolves in the latter. (Wittstein.) It likewise dissolves completely in carbonate of soda. (Herschel, *Pogg.* 25, 627.)

c. $3U^2O^2Cy,Fe^2Cy^3$?—Ferridcyanide of potassium forms with hydrochlorate of uranic oxide a copious brown-red percipitate (Gm.; Smee), which exhibits with ammonia and carbonate of ammonia the same phenomena as *b.* (Wittstein.)

Cyanides of Iron and Manganese.—*a. Ferrocyanide of Manganese.* Mn^2FeCy^3.—Ferrocyanide of potassium forms a white precipitate with [excess of] manganous salts. (In presence of cupric oxide, the precipitate has a peach-blossom colour; and if ferric oxide be present, it is bluish.)—Caustic potash converts it into hydrated manganous oxide and ferrocyanide of potassium. (Ittner.) Soluble in hydrochloric acid (Berzelius); insoluble in aqueous hydrochlorate or nitrate of ammonia. (Brett.) The precipitate contains 3 per cent. of potassium, and is, therefore, contaminated with ferrocyanide of manganese and potassium, *c.*

b. Ferridcyanide of Manganese. $3MnCy,Fe^2Cy^3$.—Ferridcyanide of potassium precipitates manganous salts in copious, delicate flakes, which are greyish brown according to Gmelin, sepia-coloured according to Smee. The precipitate becomes lighter when heated with ammonia; carbonate of ammonia acts but slightly on it; sal-ammoniac, not at all. (Wittstein, *Repert.* 63, 314.)

Manganidcyanide of potassium forms a light-blue precipitate with ferrous salts, but none with ferric salts. (Rammelsberg.)

c. Ferrocyanide of Manganese and Potassium. C^6N^3FeMnK.—Formed by dropping a manganous salt into excess of ferrocyanide of potassium. The greyish white precipitate becomes bluish grey during washing, and after the soluble salts have been washed away by the water, partly runs through the filter, forming a turbid filtrate which does not become clear by standing. (Mosander, *Berzelius Lehrb.*)

Cyanide of Iron and Arsenic ?—From a solution of arsenious acid in

hydrochloric acid, ferrocyanide of potassium throws down a white substance, insoluble in water, and decomposed by boiling nitric acid. (Ittner.)

Ferrocyanide and ferridcyanide of potassium do not precipitate *Tartar-emetic.* The white precipitate which ferrocyanide of potassium produces in acid hydrochlorate of *antimonic oxide,* appears to be nothing but powder of Algaroth; Ittner supposes it to contain a *cyanide of iron and antimony.*

Cyanides of Iron and Bismuth. — *a.* The precipitate produced by *ferrocyanide of potassium* in a solution of nitrate of bismuth is yellow at first, (white according to Berzelius, yellowish white according to Wittstein,) but afterwards becomes light green; it dissolves in nitric acid, and is precipitated from the solution by water. (Ittner.) It is precipitated of a pure white colour by ammonia and carbonate of ammonia, and at high temperatures likewise by other ammoniacal salts. (Wittstein.)

b. Ferridcyanide of potassium forms a copious light-brown precipitate with nitrate of bismuth. (Gm.) This precipitate exhibits with ammonia and its salts the same reactions as *a.* (Wittstein.)

Cyanides of Iron and Zinc.—a. Ferrocyanide of Zinc. Zn^2FeCy^3.— Formed by precipitating a zinc-salt with ferrocyanide of potassium not in excess. A boiling solution of 60 pts. (1 At.) of ferrocyanide of potassium is mixed with 83 pts. (somewhat more than 2 At.) of sulphate of zinc, and the precipitate thoroughly washed. (Schindler, *Mag. Pharm.* 36, 71.) If the ferrocyanide of potassium is in excess, part of the precipitate is redissolved; the liquid and the wash-water pass turbid through the filter; and the precipitate, while drying, smells strongly of hydrocyanic acid, does not form a very loose powder, and when treated with dilute acids, immediately gives off hydrocyanic acid. (Schindler.)—According to Mosander, the precipitate contains ferrocyanide of potassium; it is gummy, readily passes through the filter during washing, and when dry contains 12 At. water. Hence Berzelius recommends that the compound be prepared with ferroprussic acid. It is clear, however, from Schindler's analysis, that the precipitate obtained with excess of sulphate of zinc is free from ferrocyanide of potassium.

White powder, which, according to Schindler, scarcely smells of hydrocyanic acid. When heated it gives off half its water, which smells faintly of hydrocyanic acid, then hydrocyanate and carbonate of ammonia, and after very strong ignition leaves a residue of carbide of iron, carbide of zinc, and oxycyanide of zinc. If the heat applied be not sufficient to produce this complete decomposition, the residue, when sulphuric acid is poured upon it, yields a large quantity of prussian blue. It dissolves sparingly in dilute acids, but is not decomposed till boiled with them, whereupon it slowly gives off hydrocyanic acid, and yields a precipitate of prussian blue (provided nitric acid has not been used). (Schindler.) It dissolves in aqueous ammonia and in ammoniacal salts. (Wittstein; Brett.)

				Schindler.
2 Zn	64·4	32·63		32·6
Fe	28·0	14·18		13·6
3 Cy	78·0	39·51		
3 HO	27·0	13·68		
$Zn^2FeCy^3 + 3Aq$	197·4	100·00		

b. Ferridcyanide of Zinc. $3ZnCy,Fe^2Cy^3$.—Ferridcyanide of potassium forms with sulphate of zinc a brownish, orange-yellow precipitate (Gm.), which dissolves readily in ammonia and in ammoniacal salts (Wittstein.)

c. Ferrocyanide of Zinc with Ammonia.—A dilute zinc-salt, supersaturated with ammonia in a certain proportion, yields with ferrocyanide of potassium, after a few seconds, a white crystalline precipitate. If too little ammonia be added, the precipitate is mixed with pure ferrocyanide of zinc, and too much ammonia prevents the precipitation altogether. The precipitate when dry is white and very friable, sustains without decomposition a heat of 100°, and at higher temperatures gives off water and hydrocyanate of ammonia. It contains 11·50 per cent. of ammonia, 32·27 zinc, and 13·15 iron, and is, therefore, probably $2(Zn^2FeCy^3)+3NH^3+2Aq$. (Bunsen, *Pogg.* 34, 136; *comp.* Monthiers, *N. J. Pharm.* 11, 253.)

Cyanide of Iron and Cadmium.—*a.* $CdCy,FeCy^3$?—Aqueous cyanide of cadmium and potassium forms, with green vitriol, a precipitate which turns green on exposure to the air, and is not soluble in excess of cyanide of cadmium and potassium. (Rammelsberg.) Ferric sulphate and cyanide of cadmium and potassium react upon each other in such a manner as to eliminate hydrocyanic acid, and precipitate ferric oxide. (Rammelsberg.)

b. Cd^3FeCy^3?—The white precipitate which ferrocyanide of potassium produces with sulphate of cadmium, dissolves in ammonia, but not completely in ammoniacal salts, even when heated (Wittstein); in hydrochlorate or nitrate of ammonia it is insoluble. (Brett.)

c. $3CdCy,Fe^2Cy^3$?—Ferridcyanide of potassium forms with cadmic salts, a yellow precipitate (pale yellow, according to Smee), which dissolves readily in ammonia and ammoniacal salts. (Wittstein, *Reperts.* 63, 314.)

Cyanides of Iron and Tin.—*a.* Sn^2FeCy^3?—Protochloride of tin forms, with ferrocyanide of potassium, a white precipitate, which gradually turns yellow on exposure to the air, and is not soluble either in water or in acids. (Ittner.) It is insoluble in hydrochlorate and in nitrate of ammonia. (Brett.) Dissolves, but imperfectly, in ammonia and its salts. (Wittstein.)

b. $SnFeCy^3$?—Bichloride of tin forms, with ferrocyanide of potassium, a brownish yellow precipitate (white, according to Gm.), which reproduces ferrocyanide of potassium when treated with potash, and does not dissolve either in ammonia or in ammoniacal salts. (Wittstein.)

c. $3SnCy,Fe^2Cy^3$?—Ferridcyanide of potassium forms, with protochloride of tin, a white gelatinous magma (Gm.), which dissolves imperfectly in ammonia, but is insoluble in ammoniacal salts. (Wittstein.) Bichloride of tin is not precipitated by ferridcyanide of potassium. (Gm.)

Ferrocyanide of Lead. Pb^2FeCy^3.—By precipitating nitrate of lead with ferrocyanide of potassium, a white precipitate is obtained which, when washed and dried, has the composition Pb^2FeCy^3+3Aq. (Berzelius.) The precipitate, for however long a time it may have been washed, retains from 6 to 9 per cent. of ferrocyanide of potassium, of which it continues to give up a certain quantity to fresh portions of water. (Gay-Lussac.) The precipitate contains no ferrocyanide of potassium,

even if an excess of that salt has been used in preparing it, and may be easily obtained quite free from potassium by washing. (Berzelius.)

This compound, when gently heated, gives off all its water. Ignited out of contact with the air, it gives off nothing but nitrogen gas, and leaves a mixture of bicarbide of iron and bicarbide of lead, which burns like tinder when gently heated in contact with air, and when more strongly heated out of contact of air, exhibits a very bright glow; if this latter effect be produced before the cyanogen is completely decomposed, the remaining portion of nitrogen escapes with great violence. If the salt, without previous dehydration, be suddenly subjected to a strong heat, it gives off water, carbonic acid, and hydrocyanate of ammonia, leaving a residue of lead and iron, combined with a quantity of charcoal smaller than that which exists in the residue obtained by heating the anhydrous salt. (Berzelius.) The hydrated salt, when subjected to dry distillation, yields at first cyanogen gas and hydrocyanate of ammonia, and then, after exposure for a while to a red heat, suddenly exhibits a glimmering light, accompanied by rapid evolution of nitrogen. The residue, if left to cool in the retort, exhibits pyrophoric properties on exposure to the air at a temperature a few degrees above the mean; it likewise gives off a large quantity of ammonia on exposure to moist air, or when heated to redness in an atmosphere of aqueous vapour. After the combustion, there remains a yellowish brown mass, which fuses very readily before the blowpipe, and is a compound of 4 At. protoxide of lead with 1 At. sesquioxide of iron. (Gay-Lussac, *Ann. Chim. Phys.* 46, 80.) The residue left after the salt has been ignited out of contact of air, is a compound of paracyanogen with lead and iron; if it be exposed to the air while still red-hot, and especially if it be strongly blown upon, the lead is reduced over the whole surface in numerous minute drops, whose surfaces exhibit the colours of the rainbow. (Thaulow, *J. pr. Chem.* 31, 322.) Ferrocyanide of lead, heated in sulphuretted hydrogen gas, is resolved into sulphide of lead, sulphide of iron, and hydrocyanic acid (Berzelius):

$$Pb^2FeCy^3 + 3HS = 2PbS + FeS + 3HCy.$$

Ferrocyanide of lead, immersed in oil of vitriol, is converted into a white powder, which dissolves but sparingly in excess of oil of vitriol, and is precipitated from the solution by water. (Berzelius.) Sulphuretted hydrogen-water and dilute sulphuric acid eliminate ferroprussic acid from the salt, at the same time forming sulphide or sulphate of lead. The salt is not decomposed by digestion with water and carbonate of baryta or strontia. (Bette.) It is insoluble in water. It is partially soluble in hot ammonia, perfectly soluble in hot hydrochlorate or succinate of ammonia, but insoluble in other ammoniacal salts. (Wittstein.)

Dehydrated.		Berzelius.		*Hydrated.*		
2 Pb	208	66·24	65·91	2 PbO	224	65·69
Fe	28	8·92	8·81	FeO	36	10·56
3 Cy	78	24·84	23·89	3 HCy	81	23·75
Pb^2FeCy	314	100·00	98·61		341	100·00

Ferridcyanide of Lead. $C^6N^3Pb^3,C^6N^3Fe^2 = 3PbCy,Fe^2Cy^3$.—A mixture of the aqueous solutions of ferridcyanide of potassium and nitrate of lead deposits dark brown-red, translucent crystals, united in cockscomb-shaped groups, and slightly soluble in water, especially if warm. The aqueous solution deposits a bluish white powder on boiling. Dilute

sulphuric acid decomposes the compound into sulphate of lead and ferriprussic acid. (Gm.)

PROTOCYANIDE OF COBALT.—1. Hydrocyanic acid expels carbonic acid from carbonate of cobalt. (Scheele.)—2. From acetate of cobalt it throws down all the cobalt in the form of protocyanide. (Wöhler.) The solutions of protoxide of cobalt in the stronger acids are not precipitated by it.—3. Cobalt-salts are precipitated by aqueous solution of cyanide of potassium.—Pale cinnamon-coloured or dark flesh-coloured precipitate. —The compound does not give off its water at 100°; when heated to 280° in a close vessel, it gives off 32·28 per cent. (3 At.) of water, and assumes a bright blue colour. When heated in the air, it takes fire at 250°, exhibiting a bright glow, and is converted into a black porous mass. (Rammelsberg, *Pogg.* 42, 115.)—¶ According to a later observation of Rammelsberg's (*Pogg.* 73, 80), this black mass contains 6 At. cobalt, 12 At. carbon, and 1 At. nitrogen, and may be regarded as a mixture of paracyanide and carbide of cobalt. ¶—It dissolves readily in ammonia, carbonate of ammonia, and succinate of ammonia, forming yellow solutions; but in sulphate, hydrochlorate, or nitrate of ammonia, it does not dissolve completely till aided by heat. (Wittstein.) It dissolves completely in cold aqueous solution of cyanide of potassium. (Haidlen & Fresenius.) —Does not dissolve in water or in dilute acids.—¶ According to Zwenger (*Ann. Pharm.* 62, 166), this compound, after drying over oil of vitriol, contains 2 At. water:

				Zwenger.
2 Co	29·5	40·13		39·43
2 C	12·0	16·33		16·60
N	14·0	19·05		
2 HO	18·0	24·49		26·19
CoCy + 2Aq	72·5	100·00		

¶

Six-fifths Cyanide of Cobalt? $C^6N^3Co^3, C^6N^2Co^3 = 3CoCy, Co^2Cy^3$.—Cobaltidcyanide of potassium forms with salts of protoxide of cobalt, a precipitate of a beautiful rose-colour. (Gm.).—*Comp.* p. 497.

Sesquicyanide of Cobalt.—Known only in combination with other cyanides.

Hydrocobaltidcyanic Acid. $C^6N^3H^3, C^6N^3Co^3 = 3HCy, Co^2Cy^3$. — Obtained (1) by passing sulphuretted hydrogen through water in which cobaltidcyanide of lead [or of copper] is diffused, then filtering and evaporating to the crystalling point.—¶ 2. By decomposing the concentrated aqueous solution of cobaltidcyanide of potassium with a slight excess of sulphuric or nitric acid, adding absolute alcohol, and recrystallizing the mass which remains after evaporation.—Crystallizes in deliquescent, colourless, transparent needles, having a strongly acid taste. When heated above 100°, it first gives off water, then hydrocyanic acid, hydrocyanate of ammonia, and carbonate of ammonia, and at 250° leaves a blue powder, which at a higher temperature is converted into black carbide of cobalt. The aqueous solution suffers scarcely any decomposition by boiling. This acid decomposes carbonates and dissolves iron and zinc with evolution of hydrogen. It dissolves in alcohol, but is insoluble in anhydrous ether; it is not decomposed by hydrochloric acid, fuming nitric acid, or aqua-regia. When heated with oil of vitriol, it is resolved into carbonic oxide, carbonic acid,

sulphurous acid, sulphate of ammonia, and sulphate of cobalt; the addition of water before complete decomposition, gives rise to the separation of pale red cobaltidcyanide of cobalt, $Co^2Cy^6,3Co+12Aq.$, which when heated gives off water and turns blue. (Zwenger, *Ann. Pharm.* 62, 147; *Jahresber.* 1847–8, 479.)

			Zwenger (*mean*).		Or:		
2 Co	59	25·98	26·07	2 Co	59	25·98	
12 C	72	31·73	31·35	6 Cy	156	68·73	
6 N	84	37·01		3 H	3	1·32	
4 H	4	1·76	1·97	HO	9	3·97	
O	8	3·52					
$H^3Co^2Cy^6+Aq.$	227	100·00			227	100·00	

Cobaltidcyanide of Ammonium.—Obtained by neutralizing hydrocobaltidcyanic acid with ammonia. Crystallizes in colourless, transparent, oblique, four-sided tables, which are very soluble in water, and slightly soluble in alcohol. The crystals may be heated to 100° without losing weight. At about 225°, the salt begins to decompose, giving off cyanide of ammonium and carbonate of ammonia, while the residue turns blue. At a still higher temperature, it decomposes in the same manner as the blue residue of the pure acid, with which indeed it appears to be identical. (Zwenger, *Ann. Pharm.* 62, 168.)

		Zwenger.	
12 C	72	25·90	25·52
13 H	13	4·68	4·54
9 N	126	45·32	
O	8	2·88	
2 Co	59	21·22	21·30
$C^{12}N^6Co^2,3NH^4,HO$	278	100·00	

Or:

3 NH^4	54	19·41
2 Co	59	21·22
6 Cy	156	56·15
HO	9	3·22
$3NH^4Cy,Co^2Cy^3+HO$	278	100·00 ¶

Cobaltocyanide of Potassium.—Probably contained in the solution of protocyanide of cobalt in cold aqueous cyanide of potassium, inasmuch as, according to Haidlen and Fresenius, that solution gives off hydrogen when heated.

Cobaltidcyanide of Potassium. $C^6N^3K^3,C^6N^3Co^2 = 3KCy,Co^2Cy^3$. — 1. Formed by treating protocyanide of cobalt with aqueous cyanide of potassium, or carbonate of cobalt with potash and hydrocyanic acid; the action being attended with evolution of hydrogen (Gm.):

$$3KO + 2CoO + 6HCy = 3KCy,Co^2Cy^3 + 5HO + H.$$

At ordinary temperatures, the evolution of hydrogen is very slow. Recently precipitated sulphide of cobalt dissolves in hot aqueous cyanide of potassium, forming a yellow solution, which contains cyanide of cobalt and potassium and sulphide of potassium. (Haidlen & Fresenius.)— ¶ 100 pts. protocyanide of cobalt, CoCy,2HO, treated with cyanide of potassium, yielded 0·65 hydrogen. According to the equation:

$$4KCy + 2CoCy + HO = Co^2Cy^6,K^3 + KO + H,$$

the quantity should be 0·68 pt. (Zwenger.) ¶—2. By dissolving an excess of protocyanide or carbonate of cobalt, with frequent agitation, in warm aqueous potash, to which hydrocyanic acid is added in such proportion that the liquid neither reddens turmeric nor smells of hydrocyanic acid, and evaporating the filtrate to the crystallizing point. (Gm.)

Pale yellow transparent crystals, isomorphous with ferridcyanide of potassium. (Gm.)

				Zwenger.	Gm.
3 K	117·6	35·36		35·80	35·23
2 Co	59·0	17·74			17·19
12 C	72·0	21·65		21·70	
6 N	84·0	25·25			
$3KCy,Co^2Cy^3$	332·6	100·00			

Decrepitates when heated, and afterwards melts into a dark olive-green, translucent liquid, which slowly gives off bubbles. Cold oil of vitriol forms with the powder a white, pasty mass (sulphate of cobaltidcyanide of potassium), which, when heated considerably above 100°, swells up, and evolves sulphurous acid and cyanogen gases, the white mass becoming first blue, then violet, afterwards red; and finally, when heated to redness, at which temperature the excess of acid is expelled, leaves sulphate of cobalt and potash in the form of a blue transparent liquid, which when cold becomes turbid and violet-coloured, and is mixed with a white salt (excess of sulphate of potash).—The salt is not sensibly decomposed by dissolving it in hydrochloric or nitric acid, and evaporating the solution. Dissolves readily in water, forming a nearly colourless liquid, which may be supposed to contain sesqui-hydrocyanate of cobalt-oxide together with hydrocyanate of potash. Oil of vitriol added to the solution throws down the salt undecomposed, in the form of a white powder. (Gm.) ¶ According to Zwenger, however, oil of vitriol or strong nitric acid added to the aqueous solution, throws down hydrocobaltidcyanic acid; hot oil of vitriol decomposes the salt in the same manner as the acid. ¶—The solution of cobaltidcyanide of potassium does not precipitate the salts of titanic, chromic, uranic, or ferric oxide. Neither is it decomposed by alkalis. (Gm.)

¶ *Cobaltidcyanide of Sodium.* $C^6N^3Na^3,C^6N^3Co^3 = 3NaCy,Co^2Cy^3$.—Obtained by decomposing carbonate of soda with hydrocobaltidcyanic acid. The neutralization must be very exact, because the great solubility of the cobaltidcyanide of sodium renders it difficult to remove an excess either of the acid or of carbonate of soda by crystallization; free acid may, however, be removed by washing the solid salt with alcohol. Crystallizes in long, colourless, transparent needles; dissolves very readily in water, but is insoluble in alcohol. When kept for some time at 100°, it gives off all its water, and at a higher temperature fuses like the potassium-salt, into a dark-brown mass, without decomposing. (Zwenger, *Ann. Pharm.* 62, 167.)

Anhydrous.			*Hydrated.*			Zwenger.
12 C	72·0	25·27	12 C	72·0	22·44	22·44
6 N	84·0	29·48	6 N	84·0	26·18	
2 Co	59·0	20·71	2 Co	59·0	18·38	
3 Na	69·9	24·54	3 Na	69·9	21·78	21·93
			4 HO	36·0	11·22	11·25
$3NaCy,Co^2Cy^3$	284·9	100·00	+ 4Aq	320·9	100·00	

This compound, when crystallized below the ordinary temperature, appears to be capable of taking up considerably more than 4 At. water.

Cobaltidcyanide of Barium. $C^6N^3Ba^3,C^6N^3Co^3 = 3BaCy,Co^2Cy^3$.—Formed by decomposing carbonate of baryta with hydrocobaltidcyanic acid. Crystallizes in colourless, transparent prisms, which dissolve very readily in water, but are insoluble in alcohol. The crystals effloresce readily in warm air, and still more quickly at 100°. The quantity of water then given off is 22·88 p. c. (16 At.); at a higher temperature, the rest of the water, amounting to 6 At., is given off; and at a still higher temperature, the salt fuses into a dark-coloured mass, undergoing decomposition at the same time. (Zwenger, *Ann. Pharm.* 62, 169.)

Anhydrous.			*Dried at* 100°.			Zwenger.
12 C	72·0	17·12	12 C	72·0	15·17	14·26
6 N	84·0	19·97	6 N	84·0	17·70	
2 Co	59·0	14·03	2 Co	59·0	12·43	
3 Ba	205·6	48·88	3 Ba	205·6	43·32	42·81
			6HO	54·0	11·38	12·60
$3BaCy,Co^2Cy^3$	420·6	100·00	+ 6HO	474·6	100·00	

Crystallized.			Zwenger.
12 C	72·0	11·73	
6 N	84·0	13·56	
2 Co	59·0	9·51	
3 Ba	205·6	33·19	
6 HO	54·0	8·75	
16 Aq	144·0	23·26	22·88
$3BaCy,Co^2Cy^3,6HO + 16Aq$	618·6	100·00	¶

Chromidcyanide of Cobalt.—Salts of protoxide of cobalt yield a blue precipitate with sesquicyanide of chromium. (*Berzelius Lehrb.*)

Cobaltidcyanide of Manganese and *Cobaltidcyanide of Zinc.*—Manganous salts and zinc-salts yield copious white precipitates with cobaltidcyanide of potassium. (Gm.)

Cobaltidcyanide of Cadmium.—Cobaltidcyanide of potassium forms, with sulphate of cadmium, a brown precipitate, which afterwards turns white, and dissolves in excess of the cobaltidcyanide of potassium; also in acids. (Rammelsberg.)

Cobaltidcyanide of Tin.—Protochloride of tin forms a white precipitate with cobaltidcyanide of potassium. (Gm.) Bichloride of tin gives only an inconsiderable turbidity.

¶ *Cobaltidcyanide of Lead.* $C^6N^3Pb^3,C^6N^3Co^3 = 3PbCy,Co^2Cy^3$.—Obtained by decomposing carbonate of lead with hydrocobaltidcyanic acid. Crystallizes in nacreous laminæ, which dissolve very readily in water, but are insoluble in alcohol. The crystals contain 4 At. water, 3 of which are given off at 100°, and the remaining atom at 180°. (Zwenger, *Ann. Pharm.* 62, 175.)

Anhydrous, dried at 180°.			*Dried at* 100°.			Zwenger.
12 C	72	13·66	12 C	72	13·43	12·93
6 N	84	15·94	6 N	84	15·67	
2 Co	59	11·20	2 Co	59	11·01	
3 Pb	312	59·20	3 Pb	312	58·21	
			HO	9	1·68	2·09*
$3PbCy,Co^2Cy^3$	527	100·00	+ HO	536	100·00	

Air-dried.			Zwenger.
12 C	72	12·79	
6 N	84	14·92	
2 Co	59	10·47	
3 Pb	312	55·42	
HO	9	1·70	
3 Aq	27	4·70	4·51
$3PbCy,Co^2Cy^3,HO + 3Aq$	563	100·00	

Cobaltidcyanide of Lead with Oxide of Lead. $Pb^3Co^2Cy^6,6PbO,3HO$. —When ammonia is added to the aqueous solution of cobaltidcyanide of lead, this compound is obtained in the form of a white, bulky precipitate; it contains the whole of the lead, and nothing but cobaltidcyanide of ammonium remains in solution. The precipitate is insoluble in water, but soluble in acids. (Zwenger, *Ann. Pharm.* 62, 175.)

			Zwenger.
12 C	72·0	5·89	5·69
6 N	84·0	6·89	
2 Co	59·0	4·82	
9 Pb	936·0	76·27	76·19
3 H	3·0	0·24	0·57
9 O	72·0	5·89	
$Pb^3Co^2Cy^6,6PbO,3HO$	1226·0	100·00	

This compound does not, however, always exhibit the same composition; one preparation gave 72·83 p. c. lead. (Zwenger.)

Basic acetate of lead, added to cobaltidcyanide of potassium, throws down a similar compound; but the precipitation is not complete, even when an excess of the basic acetate is present. (Zwenger.) ¶

Ferrocyanide of Cobalt. $C^6N^3FeCo^2 = Co^2FeCy^3$.—Ferrocyanide of potassium forms, with cobalt-salts, a hydrated pale-blue precipitate which, even when kept from contact with the air, gradually assumes a reddish grey tint, and when carefully heated, gives off the greater part of its water, and becomes dark green. If it be then heated to 360°, it becomes light green, giving off water and a certain quantity of hydrocyanate of ammonia. When still more strongly heated in close vessels, it gives off nitrogen gas, and leaves a black mixture of carbide of iron and carbide of cobalt, which glows when raised to a higher temperature. The compound dissolves readily in oil of vitriol, forming a red liquid which, after a few hours, becomes partially decolorized and deposits sulphate of ferrocyanide of cobalt, in the form of a rose-coloured, crystalline

* The 2·09 p.c. water was driven off by heating the substance (dried at 100°) to 180°; but by combustion with chromate of lead, the quantity of water obtained was 4·41 p.c.

powder. This powder is converted by water, which abstracts the sulphuric acid, first into green anhydrous ferrocyanide of cobalt, and afterwards into the reddish-grey hydrated ferrocyanide. The latter is likewise precipitated on diluting with water the solution obtained with oil of vitriol. (Berzelius, *Schw.* 30, 50 and 59.) In aqueous caustic ammonia, the precipitate dissolves partially, and assumes a green colour; in carbonate of ammonia, a violet colour (Wittstein); it does not dissolve in solution of sal-ammoniac. (Brett.)

Ferridcyanide of Cobalt. $C^6N^3Co^3,C^6N^3Fe^3 = 3CoCy,Fe^2Cy^3$.—Protochloride of cobalt yields, with ferridcyanide of potassium, a precipitate consisting of thick dark-red flakes. (Gm.) In aqueous ammonia the precipitate assumes a rusty brown colour, but does not dissolve. (Wittstein.)

Cobaltidcyanide of Iron. $C^6N^3Fe^3,C^6N^3Co^3 = 3FeCy,Co^2Cy^3$.—The aqueous solution of cobaltidcyanide of potassium forms a copious white precipitate with ferrous sulphate. (Gm.) It does not precipitate sesquichloride of iron.

¶ *Cobaltidcyanide of Cobalt.* $C^6N^3Co^3,C^6N^3Co^3 = 3CoCy,Co^2Cy^3$.—1. Cobaltidcyanide of potassium forms, with sulphate of cobalt, a light red precipitate which may be completely freed from the potassium-salt by washing (*comp.* p. 492). The same precipitate is formed by adding hydrocobaltidcyanic acid to cobalt-salts.—2. When hydrocobaltidcyanic acid in the dry state is heated with strong sulphuric acid, and water added before the decomposition is complete (*vid.* p. 492), cobaltidcyanide of cobalt is precipitated in the form of a pale red amorphous body. The product obtained by (1) contains 14 At. water, part of which it loses at 100°, turning blue at the same time, and the rest at a higher temperature. The product obtained by (2) contains only 12 At. water; when heated it gives off water, and turns blue. Cobaltidcyanide of cobalt is perfectly insoluble in water. Caustic potash decomposes it, separating hydrated protoxide of cobalt. Ammonia dissolves it partially, forming a reddish solution, and separating a green powder. Mercuric oxide has no action upon it. The product (2) resists the action even of strong nitric and hydrochloric acid; from (1), however, strong acids extract water, and turn it blue. The anhydrous compound has a deep blue colour; in contact with moist air, it rapidly absorbs water, and turns red; when water is poured upon it, combination takes place, attended with great evolution of heat. (Zwenger, *Ann. Pharm.* 162, 172.)

	Anhydrous.		
12 C	72·0	....	23·72
6 N	84·0	....	27·68
5 Co	247·5	....	48·60
$3CoCy,Co^2Cy^3$	303·5	....	100·00

	With 12 *At. Water.*				
12 C	72·0	....	17·50	....	18·28
6 N	84·0	....	20·42		
5 Co	147·5	....	35·84	....	35·56
12 HO	108·0	....	26·24	....	27·18
$3CoCy,Co^2Cy^3 + 12Aq.$	411·5	....	100·00		

	With 14 *At. Water.*				
12 C	72·0	....	16·76	....	16·95
6 N	84·0	....	19·56		
5 Co	147·5	....	34·34	....	34·33
14 HO	126·0	....	29·34	....	28·93
$3CoCy,Co^2Cy^2$ + 14 Aq.	429·5	....	100·00		¶

CYANIDE OF NICKEL. NiCy.—1. Hydrocyanic acid decomposes acetate of nickel completely, and the neutral sulphate and nitrate partially, throwing down in each case a pale apple-green precipitate. (Wöhler.) It does not produce any precipitate in a solution of niccolo-potassic sulphate, except on addition of acetate of potash, in which case it throws down a fine white powder, soluble in excess of the hydrocyanic acid. (Gm.)—2. Aqueous cyanide of potassium forms the same precipitate with nickel-salts, and redissolves it when added in excess. (Wöhler.)

The thick, pale apple-green, hydrated precipitate obtained by (1) or (2) exhibits, after washing and drying, a leek-green colour, and a shining conchoidal fracture. The precipitate obtained with hydrocyanic acid and acetate of nickel does not give off its water—amounting to 19·025 per cent. (1½ At.)—at 100°, but between 180° and 200°. (Rammelsberg, *Pogg.* 42, 115.) Anhydrous cyanide of nickel is light brown (Berzelius); yellowish brown. (Rammelsberg.) When more strongly heated in a close vessel, it gives off nitrogen and cyanogen gases, with sudden and very bright glow, and leaves a magnetic mixture of nickel and carbide of nickel. (Wöhler.) According to Rammelsberg (*Pogg.* 73, 80), it is decomposed in the same manner as cyanide of cobalt (p. 492). Cyanide of nickel dissolves with yellow colour in the aqueous solutions of the alkaline cyanides, forming cyanogen-salts, which contain 1 At. cyanide of nickel to 1 At. cyanide of the alkali-metal, and in the dissolved state may also be regarded as compounds of hydrocyanate of nickel-oxide with hydrocyanate of the alkali. They are yellow and soluble in water. The stronger acids (not acetic acid) decompose them, with precipitation of hydrated cyanide of nickel, evolution of hydrocyanic acid, and formation of an alkaline salt. Chloride of nickel added to this solution, throws down hydrated cyanide of nickel, a chloride of the alkali-metal remaining in solution. (Wöhler.)

Hydrated cyanide of nickel dissolves quickly in caustic ammonia and carbonate of ammonia, forming a yellowish green solution (containing cyanide of nickel and ammonium and nicolate of ammonia); it likewise dissolves in warm sulphate or succinate of ammonia, and imperfectly in hydrochlorate or nitrate of ammonia. (Wittstein.)

Cyanide of Nickel and Ammonium, or *Hydrocyanate of Nickel-oxide and Ammonia*.—The yellow solution of cyanide of nickel in aqueous hydrocyanate of ammonia is partly resolved, even by spontaneous evaporation, into hydrocyanate of ammonia which escapes, and a hydrated metallic cyanide which is precipitated; but there likewise remains a certain quantity of undecomposed cyanide of nickel and ammonium in yellow needles, which when heated, first give off water, then hydrocyanate of ammonia, and leave a brown residue of cyanide of nickel; and this when more strongly heated, burns away with a glimmering light. (Wöhler.)

Cyanide of Nickel and Potassium. KCy,NiCy.—Even sulphide of nickel, when recently precipitated, dissolves in warm aqueous cyanide of potassium, forming this

compound together with sulphide of potassium. (Haidl. & Fresen.) Prepared by dissolving an excess of hydrated cyanide of nickel, with frequent agitation, in aqueous cyanide of potassium, evaporating the filtrate to the crystallizing point, and heating the crystals for some time to 100°, in order to drive off the water of crystallization.—Pale yellow; opaque.—Fuses below a red heat. When heated to redness it is slowly decomposed, giving off nitrogen and cyanogen gases, and yielding a mixture of carburetted nickel and cyanide of potassium. (Wöhler.)—Sulphuric, hydrochloric, or nitric acid, added to the aqueous solution, throws down cyanide of nickel (Wöhler), which it does not decompose without the aid of heat. (Gm.)

With water, this salt forms honey-yellow, transparent, oblique, rhombic prisms, truncated, having the obtuse summits and the acute lateral edges replaced by planes. (Wöhler.) It sometimes forms orange-yellow crystals, containing comparatively little water and giving off only 3·17 per cent. (½ At.) water at 200°, and brown-yellow crystals which contain more water and give off 6·61 per cent. (1 At.) water. (Rammelsberg, *Pogg.* 42, 114.)—Balard (*Compt. rend.* 19, 999) likewise states that the crystals contain 1 At. water.

	Dried at 200°.				Rammelsberg.
K	39·2	....	32·48	....	32·82
Ni	29·5	....	24·44	....	24·79
2 Cy	52·0	....	43·08		
$KNiCy^2$	120·7	....	100·00		

Cyanide of Nickel and Sodium.. NaCy,NiCy.—Crystallizes, in combination with water, in long six-sided prisms, which give up their water when continuously heated to 100°. The yellowish white, opaque residue melts at a stronger heat, and decomposes like the potassium-compound, but much more readily. (Wöhler.)—The crystals give off their water, amounting to 20·73 per cent. (3 At.) below 150°, and the residue contains 1 At. cyanide of potassium to 1 At. cyanide of nickel. (Rammelsberg.)

Cyanide of Nickel and Barium.—The yellow, transparent crystals give off 20 per cent. (3 At.) of water, when heated. (*Berzelius Lehrb.*)

Cyanide of Nickel and Calcium. CaCy,NiCy.—The deep yellow hydrated crystals assume when heated a pale yellow colour and micaceous aspect, and afterwards decompose, without fusion, like the potassium-compound. The aqueous solution is precipitated by alkaline oxalates and carbonates. (Wöhler.)

Cyanide of Cadmium and Nickel.—Cyanide of cadmium and potassium yields a white precipitate with sulphate of cadmium; the precipitate dissolves in excess of the potassium-compound, and in acids. (Rammelsberg.)

Cyanide of Nickel and Lead.—Aqueous cyanide of nickel and potassium mixed with acetate of lead yields, after a few days, a yellowish-crystalline powder. (Wöhler.)—White flakes, soluble in nitric acid. (F. & E. Rodgers.)

Cyanide of Nickel and Iron. FeCy,NiCy.—Aqueous cyanide of nickel and potassium forms with ferrous salts a white precipitate (Wöhler), which, after standing for some time, becomes pale blue. (F. & E. Rodgers.)

Ferrocyanide of Nickel. $C^6N^3FeNi^2=Ni^2FeCy^3$.—Nickel-salts mixed with ferrocyanide of potassium yield thick, pale apple-green flocks. These dissolve in aqueous ammonia, forming a dingy red solution (pale-

red, according to Wittstein), which, after a while, deposits silky laminæ of the same colour. (Tupputi.)—Aqueous solutions of ammoniacal salts do not dissolve this compound. (Wittstein.)—¶ When prepared as above, this compound always retains ferrocyanide of potassium, which cannot be removed by washing; the only way to obtain it pure is to decompose the following compound by boiling with water (*vid. inf.*).

Ammonio-ferrocyanide of Nickel.—*a.* $5NH^3,Ni^2FeCy^3+4HO$.—A solution of recently precipitated ferrocyanide of nickel in excess of ammonia deposits, after a short time, a violet crystalline compound, which must be dried in a current of dry ammonia. The same compound is obtained by adding ferrocyanide of potassium to the solution of a nickel-salt containing a large excess of ammonia.—In the moist state, this compound is decomposed by mere exposure to the air, ammonia and water escaping, and ferrocyanide of nickel remaining; but after drying, it does not give off water and ammonia till heated to 100° or 150°. Boiling the compound with water likewise decomposes it into ammonia, water, and ferrocyanide of nickel. Dilute acids take up the ammonia without decomposing the ferrocyanide of nickel thereby set free; strong acids decompose the ferrocyanide of nickel in the ordinary way. Potash decomposes the compound, disengaging ammonia, and forming a solution of ferrocyanide of potassium and a precipitate of oxide of nickel. (A. Reynoso, *N. Ann. Chim. Phys.* 30, 252; *Jahresber.* 1850, 358.)

b. $2NH^3,Ni^2FeCy^3,4HO$.—When ferrocyanide of potassium is added to an ammoniacal solution of nitrate of nickel, this compound is obtained in the form of a greenish white precipitate, which, after thorough drying, exhibits the appearance of a very dark green mass, becoming white by pulverization. It adheres to the tongue, is perfectly tasteless, and insoluble in water. Decomposed by heat, giving off ammonia and hydrocyanate of ammonia, and leaving a carbon-compound which burns with fusion. Weak acids decompose it in the same manner as the preceding salt, but not so easily. Ammonia dissolves it, converting it into the preceding compound *a*. Combined or rather mixed with ammonio-ferrocyanide of copper, it forms a precipitate of a beautiful peach-blossom colour. (Reynoso.) ¶

Ferridcyanide of Nickel. $C^6N^3Ni^3,C^6N^3Fe^3=3NiCy,Fe^2Cy^3$.—Nickel-salts form with ferridcyanide of potassium a thick brownish yellow precipitate (Gm.); red-brown (Smee); red-brown, becoming redder by long standing. (F. & E. Rodgers.) Identical with this compound is perhaps the reddish yellow precipitate which cyanide of nickel and potassium forms with ferric salts.

¶ *Ammonio-ferridcyanide of Nickel.* $2NH^3,Ni^3Fe^2Cy^6,HO$.—Ferridcyanide of potassium added to ammoniacal nitrate of nickel forms a beautiful yellow precipitate, soluble in excess of ammonia. (Reynoso.) ¶

Cyanide of Nickel and Cobalt. CoCy,NiCy.—Cyanide of nickel and potassium forms a pale red precipitate with cobalt-salts.

Cobaltidcyanide of Nickel. $C^6N^3Ni^3,C^6N^3Co^3=3NiCy,Co^2Cy^3$.—Cobaltidcyanide of potassium forms with sulphate of nickel-oxide and potash, fine, light, azure-coloured flakes (Gm.); according to F. & E. Rodgers, they are light green. The precipitate is not attacked by boil-

ing hydrochloric acid. (Liebig, *Ann. Pharm.* 41, 291.)—¶ According to Zwenger (*Ann. Pharm.* 62, 173), the precipitate obtained by adding cobaltidcyanide of potassium to nickel-salts, always contains cobaltidcyanide of potassium, which cannot be removed by washing. To obtain cobaltidcyanide of nickel in a state of purity, it is necessary to precipitate a nickel-salt with excess of hydrocobaltidcyanic acid. The precipitate thus obtained is gelatinous, of a light blue colour, and when exposed to the air, dries up to a transparent, greenish blue, vitreous mass, exhibiting a conchoidal fracture. It is perfectly insoluble in water and in acids. Potash-ley decomposes it, separating hydrated oxide of nickel; but ammonia dissolves it completely. Dried at 100°, it contains 12 At. water. At a higher temperature, it gives off its water, and turns grey; but the anhydrous compound, when exposed to the air, quickly absorbs a quantity of water equal to that which it has lost, and resumes its original colour. (Zwenger, *Ann. Pharm.* 62, 173.)

Anhydrous.			*Hydrated.*			Zwenger.
12 C	72·0	23·72	12 C	72·0	17·50	17·49
6 N	84·0	27·67	6 N	84·0	20·41	
2 Co	59·0	19·44	2 Co	59·0	14·34	35·43
3 Ni	88·5	29·17	3 Ni	88·5	21·50	
			12 HO	108·0	26·25	30·42
$3NiCy,Co^2Cy^3$	303·5	100·00	+12Aq	411·5	100·00	

Ammonio-cobaltidcyanide of Nickel. $2NH^3, Ni^2Co^2Cy^6 + 7Aq$. — Recently precipitated cobaltidcyanide of nickel dissolves readily in ammonia, forming a bluish solution which, when slowly evaporated, deposits the ammonia-compound in bluish crystalline scales. The compound may also be precipitated from the ammoniacal solution by alcohol; the precipitate is white at first, but when allowed to settle down quietly it assumes a bluish colour. The precipitate is amorphous, and insoluble in water. Acids withdraw the ammonia, and leave cobaltidcyanide of nickel in the form of a light blue powder. This compound undergoes no alteration when heated in the air to 100°; at a higher temperature, it takes fire, and burns away with strong intumescence. (Zwenger, *Ann. Pharm.* 62, 174.)

			Zwenger.	Or:		
12 C	72·0	17·98	18·01	$2NH^3$	34·0	8·49
8 N	112·0	27·96		3 Ni	88·5	22·10
13 H	13·0	3·25	3·44	2 Co	59·0	14·73
7 O	56·0	13·98		6 Cy	156·0	38·95
2 Co	59·0	14·73	36·19	7 HO	63·0	15·73
3 Ni	88·5	22·10				
$2NH^3,Ni^2Co^2Cy^6+7Aq$	400·5	100·00			400·5	100·00 ¶

END OF VOLUME VII.

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ERRATA.

VOL. III.

Page Line

352 — 14 from bottom; *for* Beryl, *read* Rock-crystal.

353 — 25 from top; *for* being $\frac{1}{3}$, *read* being diminished by $\frac{1}{3}$.

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383 — 10 from bottom; *for* solution, *read* compound.

386 — 7, 8 ,, The two clauses: "filtering the solution to separate the undivided iridium; dissolving the unfused black-brown mass in water;" should be *transposed*.

VOL. VII.

188 — 16 from top; *for* nitrate, *read* hydrochlorate.

210 — 4 ,, The formulæ, according to the substitution-theory, should be $C^{12}K^2Cr^2O^{24}$ and $C^8KCr^2O^{16}$.

226 — 2 from bottom; *for* acetic, *read* formic.

264 — 15 from top; *for* Dumasin, *read* resinein.

272 — 17 ,, ; *for* 70 parts, *read* 10 parts.

284 — 11 ,, ; *for* Regnault, *read* Cahours.

304 — 7 from bottom
305 — 1 from top } ; *for* Dumasin, *read* resinein.

335 — 7 ,, ; *for* 90·00, *read* 91·43.

360 — 8 from bottom; *for* $C^2N^2H^2O^2$, *read* $C^2N^2H^4O^2$.

400 — 9 ,, ; *for* red and more viscid, *read* red, viscid.

REPORT

OF

THE FIFTH ANNIVERSARY MEETING

OF THE

CAVENDISH SOCIETY.

THE Anniversary Meeting of the Cavendish Society for the year 1852 was held at the rooms of the Chemical Society, No. 5, Cavendish Square, on Monday, the 1st of March, at three o'clock in the afternoon.

The Chair was taken by THOMAS GRAHAM, ESQ., F.R.S., PRESIDENT, who called upon the Secretary to read

THE REPORT OF THE COUNCIL.

"IN reporting the result of their proceedings during the past year, the Council are again enabled to congratulate the Members on the continued prosperity and gradual extension of the Society.

"Two books have issued for 1851, namely, the first volume of LEHMANN'S 'Physiological Chemistry,' and the sixth volume of GMELIN'S 'Hand-book.' The former of these works will be completed in three volumes, the second of which is now in progress, and will constitute one of the books to be supplied to the Members this year. The sixth volume of the Translation of GMELIN'S 'Hand-book' concludes the Inorganic part of this work, in the production of which the Society has enriched the scientific literature of the country with a complete and systematic exposition of the existing state of knowledge upon the subject to which it relates. The desire to make this work generally available to British Chemists was one of the motives which originally contributed to the establishment of the Cavendish Society; and the almost unanimous

approbation, which has been expressed by the Members, of the selection which the Council made of this as their first great publication, has induced them to persist in applying nearly all the means at their command towards the completion of the Inorganic part, now finished, before undertaking other works which have been in contemplation.

"In order to meet the wishes of those who may be anxious to join the Society, with the view of possessing GMELIN'S work, the Council have arranged that the sixth volume may be substituted, when desired, for the volume of 'Chemical Reports and Memoirs,' which is out of print, as one of the books for the Subscription of 1848, by which means the six volumes of the Inorganic part of the 'Handbook,' together with the 'Life of Cavendish,' may be obtained for three years' subscription, namely, 1848, 1849 and 1850. It has been arranged also that gentlemen commencing to subscribe for 1851, may have the option of taking the 'Life of Cavendish,' instead of the sixth volume of GMELIN'S 'Chemistry,' as the book which is given in addition to the first volume of LEHMANN'S 'Animal Chemistry,' for that year.

"In the last Annual Report allusion is made to a desire which had been expressed by several Members of the Society that a Translation of BISCHOF'S 'Elements of Chemical and Physical Geology' should be undertaken by the Council at as early a period as possible. The attention of the Council had previously been directed to this work, but, notwithstanding the high reputation it had acquired among scientific men, and the general interest of the subject, it was thought to be too voluminous to admit of its being undertaken while other extensive works were in hand. An arrangement has subsequently been made with the author which has removed the difficulty the Council had previously felt, and it is now decided that PROFESSOR BISCHOF shall rewrite the work for the Society in a more condensed form, and at the same time introduce such new facts and views as he may have acquired from recent observations. The preparation of this work is now in progress, and the first volume will be supplied to the Members in the course of the present year.

"The Organic part of GMELIN'S 'Hand-book of Chemistry' is also being prepared for publication."

TREASURER'S STATEMENT of the RECEIPTS and EXPENDITURE of the CAVENDISH SOCIETY, from the 1st of March, 1851, to the 26th of February, 1852.

RECEIPTS.			£	s.	d.
Balance from previous year			407	3	11
70	Subscriptions for	1848	41	3	6
60	Ditto	1849	62	6	0
112	Ditto	1850	116	18	0
616	Ditto	1851	646	2	0
32	Ditto	1852	33	12	0
			£1307	5	5

EXPENDITURE.	£	s.	d.
Stationery, Postage, Delivery of Books ..	24	15	6
Boxes for Books	10	5	3
Advertisements	1	5	6
Insurance	2	5	0
Collector's Commission	8	17	6
Secretary	85	0	0
Editorial expenses	255	0	0
Paper	212	0	0
Printing	222	13	0
Engraving and Printing Engravings ..	10	3	0
Binding and wrapping	134	8	5
	966	13	2
Balance in hand	340	12	3
	£1307	5	5

We have examined the above statement, and find it correct.

P. N. JOHNSON.

J. E. BOWMAN.

It was moved by Dr. John Stenhouse, seconded by Mr. Edmund Greaves, and resolved,

"That the Report just read be received and adopted."

The Meeting then proceeded to the election of Officers for the ensuing year, and the following Gentlemen were declared to have been duly elected:—

President.

Professor Graham, F.R.S.

Vice-Presidents.

Arthur Aikin, F.G.S.
Professor Brande, F.R.S.
Earl of Burlington, F.R.S.
Sir James Clark, M.D., F.R.S.
Walter Crum, F.R.S.
John Davy, M.D., F.R.S.
Michael Faraday, D.C.L., F.R.S.
J. P. Gassiot, F.R.S.
Sir. R. Kane, M.D., F R.S.
W. A. Miller, M.D., F.R.S.
Jonathan Pereira, M.D., F.R.S.
Professor Wheatstone, F.R.S.

Council.

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Jacob Bell, M.P., F.L.S.
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J. E. Bowman, F.C.S.
P. J. Chabot, M.A., F.R.A.S.
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Treasurer.

Henry Beaumont Leeson, M.D., F.R.S., St. Thomas's Hospital.

Secretary.

Theophilus Redwood, Esq., 19, Montague Street, Russell Square.

It was moved by MR. WILLIAM BASTICK, seconded by MR. WILLIAM GLASS, and resolved,

"That MR. T. H. HENRY, MR. TESCHEMACHER, and DR. PERCY, be appointed Auditors for the ensuing year."

The following Resolutions were unanimously adopted:—

"That the thanks of the Meeting be given to the PRESIDENT, TREASURER, and COUNCIL, for their services to the Society."

"That the thanks of the Meeting be given to the HONORARY LOCAL SECRETARIES for their services to the Society."

"That the thanks of the Meeting be given to the CHEMICAL SOCIETY for the use of their rooms on the present occasion."

The Meeting was then adjourned.

THEOPHILUS REDWOOD, SECRETARY,
19, Montague Street, Russell Square.

MARCH 1ST, 1852.

WORKS OF THE CAVENDISH SOCIETY.

1848.

1.—CHEMICAL REPORTS AND MEMOIRS. Edited by THOMAS GRAHAM, F.R.S. (Out of Print.)

2.—HAND-BOOK OF CHEMISTRY. By LEOPOLD GMELIN. Translated by HENRY WATTS, B.A., F.C.S. Vol. I.

1849.

3.—HAND-BOOK OF CHEMISTRY. By LEOPOLD GMELIN. Vol. II.

4.—HAND-BOOK OF CHEMISTRY. By LEOPOLD GMELIN. Vol. III.

5.—THE LIFE AND WORKS OF CAVENDISH. By Dr. GEORGE WILSON.

1850.

6.—HAND-BOOK OF CHEMISTRY. By LEOPOLD GMELIN. Vol. IV.

7.—HAND-BOOK OF CHEMISTRY. By LEOPOLD GMELIN. Vol. V.

1851.

8.—PHYSIOLOGICAL CHEMISTRY. By PROFESSOR LEHMANN. Translated by GEORGE E. DAY, M.D., F.R.S. Vol. I.

9.—HAND-BOOK OF CHEMISTRY. By LEOPOLD GMELIN. Vol. VI.

1852.

10.—HAND-BOOK OF CHEMISTRY. By LEOPOLD GMELIN. Vol. VII. (Organic Chemistry, Vol. I.)

11.—PHYSIOLOGICAL CHEMISTRY. By PROFESSOR LEHMANN. Vol. II.

12.—ATLAS OF PLATES RELATING TO PHYSIOLOGICAL CHEMISTRY. By DR. OTTO FUNKE.
(Supplement to LEHMANN'S PHYSIOLOGICAL CHEMISTRY.)

The first of the Society's publications, the volume of CHEMICAL REPORTS AND MEMOIRS, being out of print, those who now join the Society, and desire to obtain the whole of GMELIN'S CHEMISTRY, may be supplied with the first volume of this work on payment of half the Subscription for 1848; or the sixth volume of the HAND-BOOK OF CHEMISTRY may be substituted for the CHEMICAL REPORTS AND MEMOIRS as one of the books for 1848, so that the six volumes of GMELIN'S CHEMISTRY and THE LIFE OF CAVENDISH may be obtained for three years' subscription, namely, 1848, 1849, and 1850. Members commencing from 1851 have the option of taking THE LIFE OF CAVENDISH instead of the sixth volume of GMELIN'S CHEMISTRY as the book which is given in addition to the first volume of LEHMANN'S PHYSIOLOGICAL CHEMISTRY for that year.

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